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MODELING OF GASEOUS $^{14}CO_2$ RELEASE FROM PERFORATIONS IN SPENT FUEL DISPOSAL CONTAINERS

C. Pescatore and T.M. Sullivan

November 1991

DEPARTMENT OF NUCLEAR ENERGY
BROOKHAVEN NATIONAL LABORATORY, ASSOCIATED UNIVERSITIES, INC.
UPTON, NEW YORK 11973

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NUCLEAR WASTE AND MATERIALS TECHNOLOGY DIVISION
DEPARTMENT OF NUCLEAR ENERGY
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ABSTRACT

The potential release of gaseous $^{14}CO_2$ from small perforations in spent fuel containers has been evaluated as a function of temperature, hole size, effective porosity of corrosion products within the hole, and time, based on the waste package design parameters and environmental conditions described in the Yucca Mountain Site Characterization Report (SCP). The SCP does not specify initial fill gas (argon) pressure and temperature. It is shown that, if significant ^{14}C oxidation takes place during the initial, inert-gas phase, an incentive exists to initially underpressurize the containers. This will avoid large, spiked releases of gaseous $^{14}CO_2$ and will result in delayed, smaller, and more uniform release rates over time. Therefore, larger size perforations could be tolerated while meeting the applicable regulations.

EXECUTIVE SUMMARY

The potential release of gaseous $^{14}CO_2$ from small perforations in waste containers has been evaluated as a function of temperature, perforation radius, open porosity within the perforation, and time, based on the waste package design parameters and environmental conditions described in the Yucca Mountain Site Characterization Plan (SCP). The SCP does not specify the initial fill gas (argon) pressure and temperature. Therefore these parameters were treated as design variables.

The analysis has been performed by breaking the release problem into two time domains. In the first time domain a positive ΔP between the argon fill gas and outside air drives the former out of the spent fuel container (type-1 conditions). Experimental evidence shows that, except for very small, inconsequential perforations, the flow regime is essentially of the Poiseuille type for compressible gases. By the time equilibration of the inside and outside pressure is achieved, 30 to 50% of the argon gas and of the $^{14}CO_2$ inventory (modeled as an impurity in the argon gas) are released. Equilibration will take less than a year for perforations larger than 35 μm in radius. For these perforations the release of $^{14}CO_2$ can be characterized as a spiked release. Equilibration times are not very sensitive to failure time indicating that in this flow regime the rate of temperature decrease with time is not a controlling factor.

ΔP-driven flows are problematic in that relatively small perforations allow release rates that exceed regulatory limits. This is demonstrated in Figure 12 (p. 39), where it is shown that, following the oxidation of 1% of the total ^{14}C inventory in the spent fuel, the ΔP-driven flow of ^{14}C from a 5-μm radius perforation results in release rates which exceed the fractional release rate criterion of 10^{-5}/year set forth in 10 CFR 60.

Following pressure equilibration, air is assumed to be the new fill gas instantly oxidizing the exposed ^{14}C. In this time domain $^{14}CO_2$ counterdiffuses against the inflow of air leaking into the container in order to offset the natural decrease in pressure due to the decay in the temperature field (type-2 conditions). The inflow of air is especially significant for perforations of 100-μm radius and smaller, and it is most important at early times. This is illustrated in Figure 11 (p. 38) where, for failure at 15 years, the inflow of air greatly reduces the

release of ^{14}C. This type of flow regime is characterized by relatively uniform releases over time. The present analysis of this flow regime significantly improves on previous ones, in that the air inflow velocity is properly accounted for as a function of hole size and temperature along with ^{14}C depletion effects. The final results suggest allowable perforation sizes, in terms of the NRC regulations, at least an order of magnitude greater than previously estimated based solely on ΔP-flow (type-1 conditions).

In both time domains conservative assumptions were implemented regarding modeling itself and the environmental parameter values which were used. For example, a temperature profile was considered which is more typical of the hottest containers.

The $^{14}CO_2$ release models presented in this report can and should be used for analyzing the potential of present container designs to meet the EPA and NRC regulations. An important conclusion already apparent from the present work is that, if indeed significant oxidation of the ^{14}C takes place during the high-temperature phase, an incentive exists to originally underpressurize the containers so that a negative ΔP will always exist at time of breach. This will ensure that type-2 conditions will prevail avoiding spiked releases, removing small size perforations (35-μm radii and smaller, say) from the list of potential offenders, and resulting in the smallest releases at early times when the release criteria are strictest. Alternatively, the present analysis helps provide the basis for requesting changes in the regulations if it is found impossible to demonstrate with reasonable assurance that the perforation area will be limited to such low levels as the present regulations require.

In any event, it is also recognized that the release rate limits on ^{14}C from a HLW repository are extremely stringent and not in line with the criteria applicable to other phases of the nuclear fuel cycle. Our preliminary findings suggest that it should be possible to request a relaxation of the EPA release criterion for ^{14}C by one order of magnitude or slightly more. This could allow up to 100% of the ^{14}C inventory in the HLW to be released to the accessible environment without licensing penalties. Accordingly, this would eliminate or reduce the need for a detailed prediction of perforation sizes in order to estimate potential $^{14}CO_2$ releases.

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1. INTRODUCTION

In recent years, the potential release of ^{14}C from failed spent fuel containers at Yucca Mountain has become an important licensing concern [Van Konynenburg, 1985 and 1987], [Oversby, 1987], [Liepens, 1988], [Ross, 1988], [Pescatore, 1989 and 1990], [Pigford, 1989], [Smith, 1989], [Knapp, 1990], [Park, 1990], [Quan, 1990], [Zwahlen, 1990]. This is due to the very small releases which the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) high-level waste regulations allow.

According to the EPA rule presently under review, the *cumulative* release of ^{14}C from any HLW repository to the accessible environment should not exceed 0.1 Ci per metric ton of heavy metal (MTHM) over 10,000 years after disposal [EPA, 1985]. This corresponds to a maximum cumulative release of roughly 7,000 Ci, i.e., an average rate of release of 0.7 Ci/yr, from the proposed repository. The latter is a very small rate considering that ^{14}C is likely to be released from spent fuel in gaseous form, mostly as $^{14}CO_2$, [Van Konynenburg, 1985] and that, according to German data, routine releases of gaseous ^{14}C compounds to the environment from the stacks of nuclear power plants amount to roughly 5.6 Ci/yr for 1 GW(e) PWRs and 13.5 Ci/yr for 1 GW(e) BWRs [NCRP, 1985; p. 17].

The NRC rule [NRC, 1983] limits the release <u>rate</u> of ^{14}C during the controlled release (CR) period to no more than 1 part in 10^5 per year of the ^{14}C inventory at 1,000 years or, alternatively, to no more than 1 part in 10^8 of the total curie inventory of the waste present at 1,000 years. According to the first criterion, considering a ^{14}C inventory at 1,000 years of about 1.37 Ci/MTHM (based on PWR fuel with 33,000 MWd/MTHM burnup and BWR fuel with 27,500 MWd/MTHM burnup [Roddy, 1986]†) and 70,000 MTHM‡ of spent fuel waste to be disposed of, one obtains a maximum release rate of roughly 1 Ci/yr. Based on a total waste inventory of 1,730 Ci/MTHM at 1,000 years, the alternate criterion

---

† More recent estimates by Van Konynenburg [Van Konynenburg, 1990], indicate a ^{14}C activity of 0.97 Ci/MTHM at 1,000 years. These data will also be referred to later in the body of the text.

‡ The waste acceptance criteria in the DOE Mission Plan [DOE, 1988a] specifies only 63,000 MTHM of spent fuel with the remaining 7,000 MTHM in glass waste forms. ^{14}C release from glass waste forms is believed to be negligible, therefore, use of 70,000 MTHM is conservative as it overestimates inventories by 10%.

allows instead a maximum release rate from the proposed repository of 1.2 Ci/yr.

A third and more stringent criterion is the NRC's requirement of substantially complete containment (SCC) of all radionuclides within the waste package for a minimum period of time between 300 and 1,000 years after closure of the underground facility. No numerical statement of allowable releases during the SCC period is provided. It has been proposed by the DOE [DOE, 1988] that release rates during the SCC period be set 10 times lower than the controlled release rate limits. This would result in a maximum, allowable release rate of roughly 0.06-0.1 Ci/yr from the proposed repository during the SCC period.

Because a relatively large fraction of the ^{14}C in a spent fuel container may be available for rapid gaseous release, the above release rate criteria pose very strict requirements on container performance and may drive container design considerations*.

Credit for meeting the regulatory criteria may be sought by observing that:

1. all of the ^{14}C inventory may not be available for release at time of breach or later**;

2. there may be significant mass transfer resistance to release through the openings in the container wall; and

3. there will be a time distributed failure rate of spent fuel containers.

This report addresses some of the issues relevant to item 2. In particular, we examine the most significant transport mechanisms of gaseous $^{14}CO_2$ through containers with single or multiple perforations and provide expressions to evaluate potential releases. Numerical

---

* Assuming, for the sake of simplicity, that all waste packages contain 6 PWR 17x17 spent fuel assemblies, one obtains a ^{14}C inventory of 4.285 Ci (based on Roddy's inventory data) per container at time of disposal and a total number of 25,285 containers. Thus the allowable yearly releases from the whole repository correspond to roughly one fortieth or less of the initial ^{14}C inventory of a <u>single</u> container.

** Indeed, with the hypothesis that no more than roughly 6% of the ^{14}C is available for release as $^{14}CO_2$ over a 10,000 year period, the EPA criterion for cumulative release would be met automatically regardless of the container failure rate.

examples are also provided. The main conclusion of the report is that underpressurization of the original spent fuel containers should be considered in order to help meet the regulatory criteria and to ensure relatively slow, uniform releases in case of breach.

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2. REFERENCE DATA AND CONSTITUTIVE LAWS

2.1 Data

In order to examine the mass transfer problem of ^{14}C through openings in waste containers, a typical spent fuel container loaded with intact fuel waste is envisioned with relevant properties taken from the Yucca Mountain Site Characterization Plan (SCP) [DOE, 1988]. Namely:

wall thickness $\ell = 1$ cm ,

gas volume $V = 1\ m^3$.

The fill gas is argon, with mass number 39.95. For later use we observe that, by least-square fitting the data of Table I, the viscosity of argon as a function of temperature can be represented as follows:

$$\mu(T) = 208.72 + 0.9378\ T - 0.1299\ T^{1.2} \qquad (1)$$

with $[\mu]=[\text{micropoise}]$ and $[T]=[^{o}C]$. The self-diffusion coefficient of argon is estimated from Fuller's correlation [Reid, 1987] and is expressed as follows:

$$D(\vartheta,P) = 8.836\cdot 10^{-6}\cdot \frac{\vartheta^{1.75}}{P}, \qquad cm^2/s, \qquad (2)$$

with $[\vartheta]=[^{o}K]$ and $[P]=[\text{atm}]$.

Table I Absolute viscosity of argon as a function of temperature. [CRC, 1981; p. F-58]

T [^{o}C]	$\mu\cdot 10^6$ [poise]
20	221.7
100	269.5
200	322.3
302	368.5

Also needed for later use are the average temperature of the gas in the container and the temperature of the container wall. The latter is shown in Figure 1 ("canister O. D.") taken from the Yucca Mountain SCP. The functional dependence on time is estimated to be as follows:

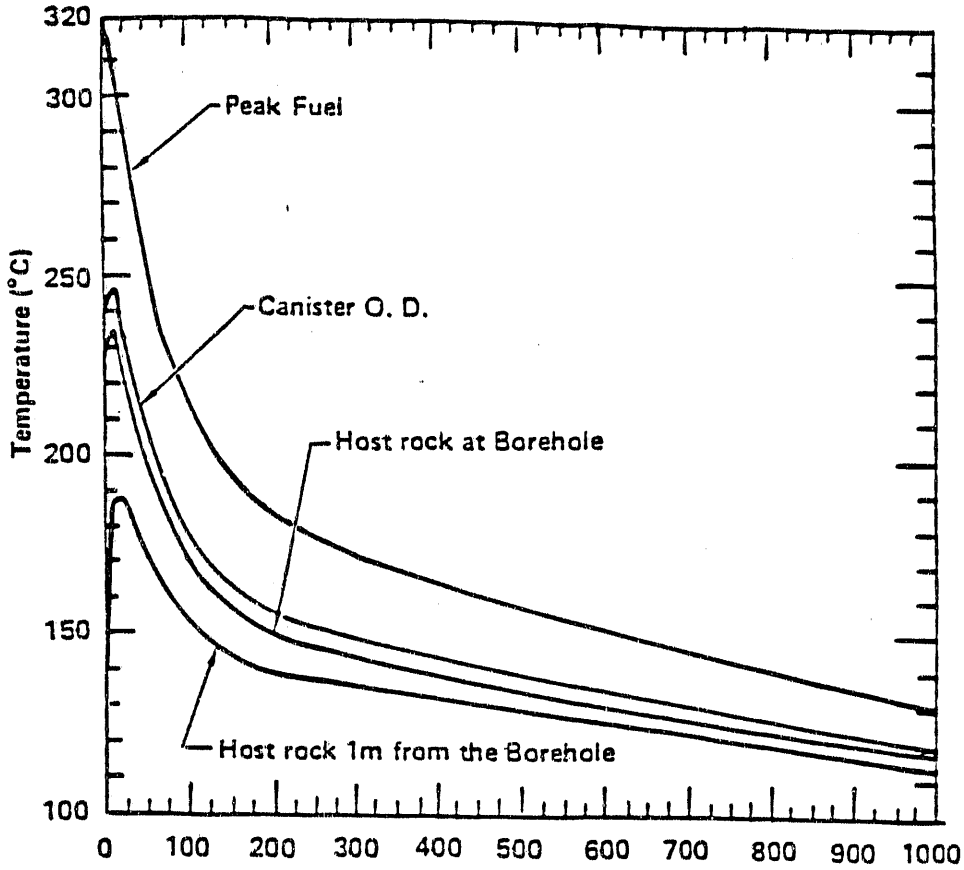
$$T_w(t) = 92.774 - 0.0189\ t + 359.08\ t^{-0.3}, \quad t \geq 15\ yr \qquad (3)$$

with $[T_w]=[^{\circ}C]$ and $[t]=[yr]$. This temperature curve only applies to the hottest containers. Containers placed farther away from the center of the repository are expected to exhibit a lower initial temperature increase (edge effects). Furthermore, the validity of Equation (3) cannot be extended much beyond its range of interpolation of the data, 1,500 years say, as it may yield unrealistic results. On the other hand it is the relatively early failures that cause most concern both because the release rate criteria are strictest at those times and because the oxidation rate of ^{14}C in air is larger the higher the temperature [Smith, 1989].

The *average* temperature of the gas within the waste container is not known. No internal temperature calculations of the present SCP waste package designs are available [Sullivan, 1989] (the internal temperature profile of Fig. 1 refers to a design no longer under consideration). By examining the more detailed work performed in the allied field of dry storage of spent fuel [Sullivan, 1989], we have *judged* that the ratio of the average gas temperature expressed in degrees Kelvin, ϑ_b, to the wall temperature expressed in degrees Kelvin, ϑ_w, should be of the order of 1.1 or less. Accordingly, in the remainder of the report we approximate $\vartheta_b(t)$ as follows:

$$\vartheta_b(t) = 1.1\ \vartheta_w(t) \qquad (4)$$

The SCP does not indicate a reference argon fill pressure or temperature. Thus these two variables are left open as design parameters. We assume, however, that enough argon is utilized that the oxidized ^{14}C fraction available for release at any time can be considered as an impurity in the fill gas. This assumption is justified by noticing that even if the total ^{14}C inventory of a container (4.285 Ci) were to be oxidized into $^{14}CO_2$ its partial pressure would amount to only 0.002 atm at room temperature and that, in practice, only a few percent of the initial ^{14}C inventory will be present as $^{14}CO_2$ in a container at any time. Under these conditions the mean free path



Time after emplacement (years)

WF.....PWR.SF

LPD.....57.0

APD.....48.4

10yr PWR-AVE.....3.3KW

C_{Diam}.....0.7m

P_{PKG}.....5m

P_{DRIFT}.....46.86m

Directory No.....P57V3.3A

Figure 1. Temperature histories, presented in the SCP, assuming vertical emplacement of the spent fuel containers [DOE, 1988].

(mfp)[1a] of $^{14}CO_2$ will be the same as the mfp of the fill gas, be it argon at the time of container failure or air later on[1b]. In the hard-sphere kinetic theory of gases with Maxwellian distribution of velocities the mfp of a single-component gas is defined as :

$$mfp = \frac{1}{1.414\ \pi\ d^2\ n} \tag{5}$$

with n=number of gas molecules per unit volume, d=molecular diameter. The mfp of a hard-sphere Maxwellian gas at constant density has no dependence on temperature. For argon at 1 atm and 0 ^{o}C the mfp is reported [CRC, 1981] to be $(mfp)_{Ar} = 6.20 \cdot 10^{-8}$ μm. A similar value should be expected for the mfp of air, as the molecular diameter of air is only 1.02 times that of argon [Kennard, 1938][2a].

2.2 Constitutive laws

2.2.1 ΔP-driven flows

Any time a pressure gradient and pathway exist between the interior and the exterior of the container, flow may occur. Hedley [Hedley, 1978] experimentally determined the flow rate of air, helium, and helium-air mixtures through cylindrical holes for mean pressures between 1 and 2 atm, ΔPs between 0.1 and 4 atm, diameters of 1 to 60 μm, length-to-diameter ratios greater than 100, and a temperature of 30 ^{o}C. Under those conditions, Hedley found that for opening diameters greater than 5 μm the experimental flow rates are correctly predicted by the Poiseuille law for compressible gases. For opening diameters between 0.6 and 1.7 μm, the experimetal flow rates exceeded those predicted by the Poiseuille law by approximately a factor of 3. No explanation was given for this flow increase.

1a "The concept of mean free path is intuitively appealing ... but it does not appear in modern kinetic theory" [BSL, 1960]. Modern kinetic theory takes into account the long-range forces that gas molecules exert on one another. We rely on the concept of mfp because it is used commonly to discern between the various types of gas flow regimes.

1b Zwahlen et al. [Zwahlen, 1990] appear to have overlooked this point.

2a Kennard also reports the molecular diameter of CO_2 to be 1.26 times that of argon.

The Poiseuille law for compressible gases applies when the gas mfp is less than about one percent of the hole diameter [Perry, 1984; pp. 5-28 to -33] and it presumes laminar, isothermal, fully-developed flow between two infinite reservoirs connected by a cylindrical duct. Mathematically this law is expressed as follows:

$$Q = \frac{\pi r^4 \quad (\Delta^2 P)}{16 \mu(T) \ell R T} \tag{6}$$

with:

$\mu(T)$ - temperature-dependent absolute viscosity of the gas
ℓ - length of the opening
R - the universal gas constant
$\Delta^2 P = (P_1^2 - P_2^2)$ - P_1, P_2 absolute upstream and downstream gas pressures
r - radius of the opening
T - flow-field temperature

With the appropriate units Q is expressed in turn as number-of-moles/unit-time.

At the time a spent fuel container develops a breach, it is likely that a ΔP will exist between the interior and the exterior of the container and that the internal pressure will tend to equalize, in time, to the external pressure. Based on Hedley's results it seems reasonable to assume the applicability of Poiseuille law for the problem at hand provided that one considers hole diameters in the range of five to a few hundred microns and that one regards the release problem as a succession of isothermal states during which the temperature is practically constant and no significant depletion (accumulation) of interior gas species takes place. This is indeed the case as it is realized *a posteriori* when one compares the time needed for significant change in temperature and in gas inventories with the time needed, experimentally, to achieve Poiseuille flow.

When the mfp has a value between 1 and 65 percent of the channel diameter a correction term must be added to Poiseuille law [Perry, 1984]. This correction is known as the viscous slip term and can be represented analytically as follows [Scott, 1962]:

$$\text{viscous slip correction} = \frac{32\ \text{mfp}}{9\ r} \cdot Q \qquad (7)$$

with Q given by Equation (6). With our values for the mfp's of argon and air, the viscous slip correction has to be factored in for opening diameters between 0.1 and 6 microns, roughly. In practice, it is a relevant term only when modeling porous flow [Youngquist, 1970].

When the mfp is greater than about 65% of the channel diameter Knudsen flow becomes the dominant transport mechanism. Because, in our situation, Knudsen flow would require opening diameters of less than 0.1 μm, we are <u>not</u> interested in this flow regime[2b]. In any event, the $^{14}CO_2$ release rate will be negligible in openings this small.

2.2.2 Concentration-driven flow

Along with pressure-driven flows, diffusion will cause mass transport through the container wall when a pathway and a difference in concentration exist between the inside and the outside of the container. For a gas with molar concentration N inside the container and zero concentration outside, the steady-state release from a cylindrical hole can be computed as follows [Aidun, 1987]:

$$J_D = \frac{D\ N}{\ell + 0.25\ \pi r} \qquad (8)$$

With the appropriate units, the quantity J_D is measured as moles/unit-time/unit-area. There will always be some argon (or CO_2) in the air outside of the container. Thus, the assumption of zero concentration outside of the container is conservative because because it predicts higher release rates than those that will occur.

The self-diffusion coefficient of argon as a function of pressure and temperature is given by Equation (2). The equivalent expression for the binary diffusion coefficient of $^{14}CO_2$ in air estimated from Fuller's correlation [Reid, 1987; pp. 587-589] is:

2b The analysis of ^{14}C release under ΔP-driven flow conditions performed by Zwahlen [Zwahlen, 1990] implements the Poiseuille law, ignores viscous slip, and evaluates Knudsen flow outside the proper range of applicability.

$$D(\vartheta,P) = 7.381\cdot 10^{-6} \cdot \frac{\vartheta^{1.75}}{P}, \qquad cm^2/s, \tag{9}$$

with $[\vartheta]=[^{o}K]$ and $[P]=[atm]$.

It seems reasonable to assume the applicability of Equation (8) for the problem at hand provided that one regards the release problem as a succession of approximately isothermal states during which no significant depletion (accumulation) of interior gas species takes place. This is indeed the case as the high values of the gaseous diffusion coefficients promote a rapid establishment of steady state conditions compared with the time needed for significant change in temperature and in gas inventories.

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3. MODELING OF GASEOUS RELEASE FROM THE SPENT FUEL CONTAINERS

In order to be able to model ^{14}C release from failed spent fuel containers we subdivide the problem into two time domains. In the first time domain the internal fill gas (argon) pressure, assumed to be higher than the outside pressure, tends to equilibrate with the external pressure. As soon as equilibration is achieved, air is assumed to rapidly flow into the container and serve as the new fill gas. At this time the new time domain begins. The assumption that air becomes the new fill gas upon pressure equilibration is conservative because it provides an instant source of oxygen to oxidize the ^{14}C on the cladding. In this second phase we are interested in the interplay between the outward diffusion of a gaseous impurity, i.e., $^{14}CO_2$, and the inflow of air needed to compensate for the internal pressure decrease due to the decaying temperature field.

In the first time domain the counterdiffusion of oxygen (which could further oxidize the ^{14}C inventory of the cladding) against the argon flow is neglected, because our calculations suggest that, during this early phase, the argon outflow velocity is high enough to practically annul the counterdiffusion process.

3.1 Time to equilibration

3.1.1 Fully open perforations

The ideal gas law provides an expression that relates the temperature, pressure, and number of moles in one container:

$$PV = nRT \tag{10}$$

The total derivative of pressure with respect to time consists of an isothermal and an iso-mass term. Namely:

$$\frac{\partial P}{\partial t} = \frac{R\,T}{V} \cdot \left.\frac{\partial n}{\partial t}\right|_T + \frac{R\,n}{V} \cdot \left.\frac{\partial T}{\partial t}\right|_n \tag{11}$$

The term $(\partial n/\partial t)_T$ represents the molar change at constant temperature and corresponds to the loss of argon due to Poiseuille and diffusive flow; viscous slip will be neglected as we shall not consider fully open

perforations of smaller diameter than 10μm. The second term represents the change in pressure in a closed system due to a change in temperature. Thus, after recasting all contributions in terms of the gas pressure, P, inside the container, one obtains the following mass balance equation:

$$\frac{\partial P}{\partial t} = - \frac{1.1\ \pi r^4\ (P^2 - P_o^2)}{16\ \mu(t)\ \ell\ V} - \frac{D(t)\ P\ \pi r^2}{V\ (\ell + 0.25\ \pi r)} + \frac{P}{T(t)} \cdot \frac{\partial T}{\partial t} \qquad (12)$$

Equation (12) forms the basis of our calculations regarding time to equilibration. In it the multiplicative factor of 1.1 is obtained from Equation (4), while P_o represents the external, average pressure. The temperature profile to be used is that given by Equation (3) expressed in degrees Kelvin. All terms in Equation (12) depend on temperature to some extent. As we shall see later, the temperature at failure plays an important role in determinining the time to equilibration and amount of fill gas released. For smaller holes and for early failures the temperature rate of change with time is also important.

A further quantity of interest is the flow velocity, u. Based on Poiseuille law, the latter quantity can be expressed now as follows:

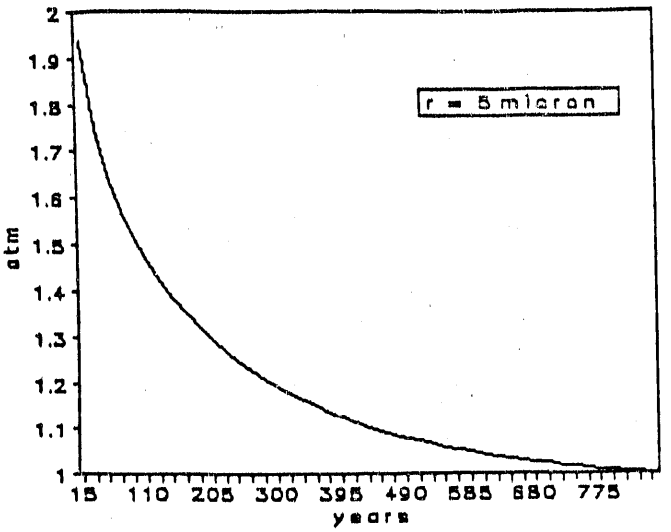
$$u = \frac{1.1\ r^2\ (P^2 - P_o^2)}{16\ \mu(t)\ \ell\ P} \qquad (13)$$

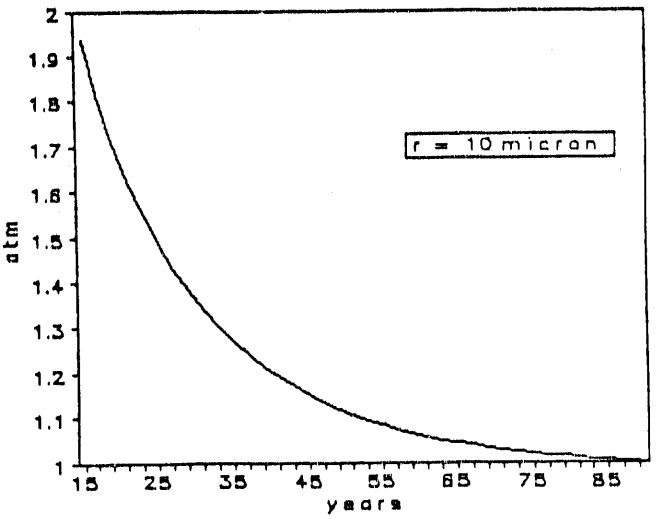
Figures 2 through 5 show the results of a set of calculations for hole radii of 5, 10, and 30 microns with breach starting at 15 years after closure. For all these cases the fill pressure is assumed to be 1 atm at 25 ^oC and the external pressure is assumed to be 1 atm[3a]. In particular, Figures 2 through 5 report the evolution of the internal pressure with time as well as (a) the fractional molar rate of argon loss per year[3b] (b) the flow velocity in the opening, (c) the

---

3a The Yucca Mountain proposed repository is at roughly 1,100 m above sea level. At this elevation, the average pressure is roughly 0.9 atm. Future calculations may want to consider this as the reference pressure. Our calculations indicate that the trends presented in this report will not differ significantly if this value of the pressure is used instead of 1 atm.

3b The fractional release rate of $^{14}CO_2$ is the same as that of argon. In order to normalize this rate to the total ^{14}C inventory one has to multiply this curve by the oxidized fraction, f. Zwahlen et al., for instance, take f to be 1%.





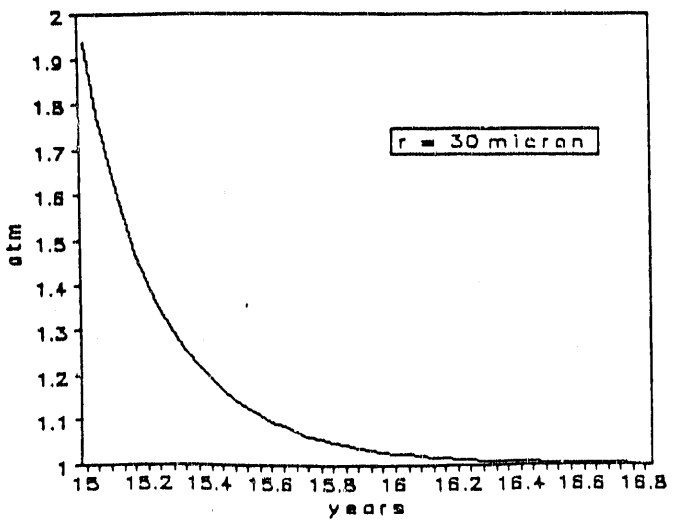
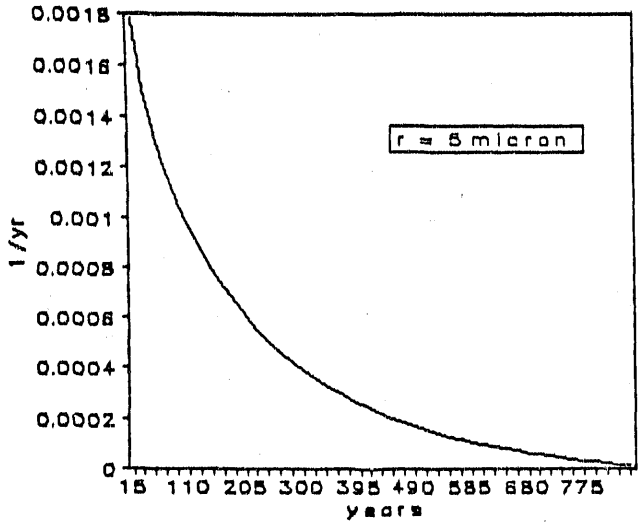
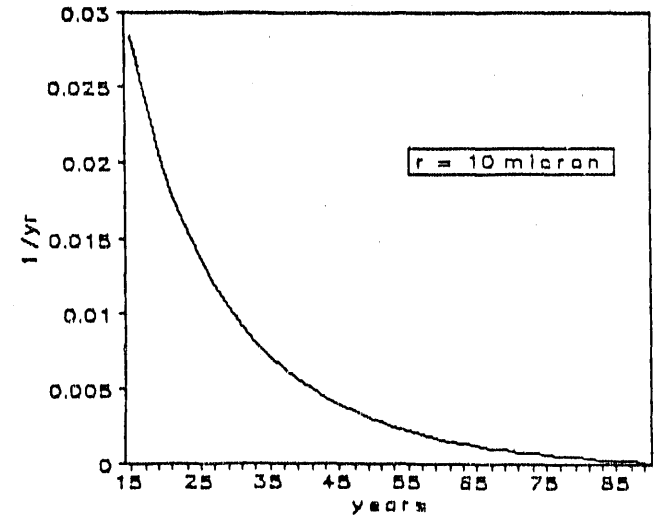


Figure 2. Internal pressure decay for 5, 10, and 30 μm radius perforations with breach occurring at t = 15 years.





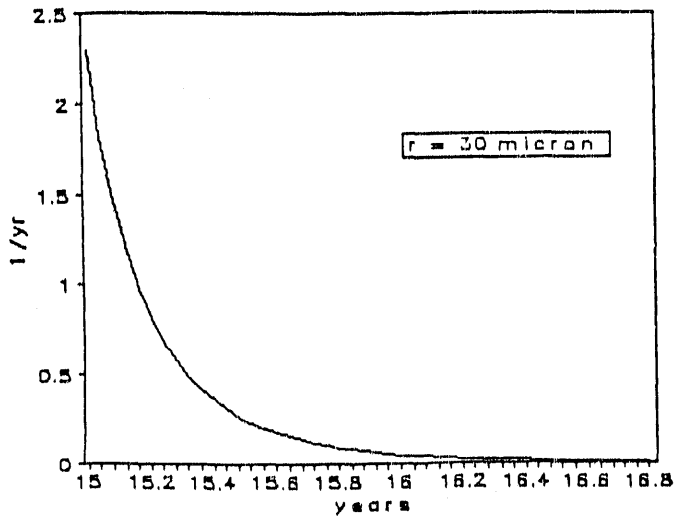
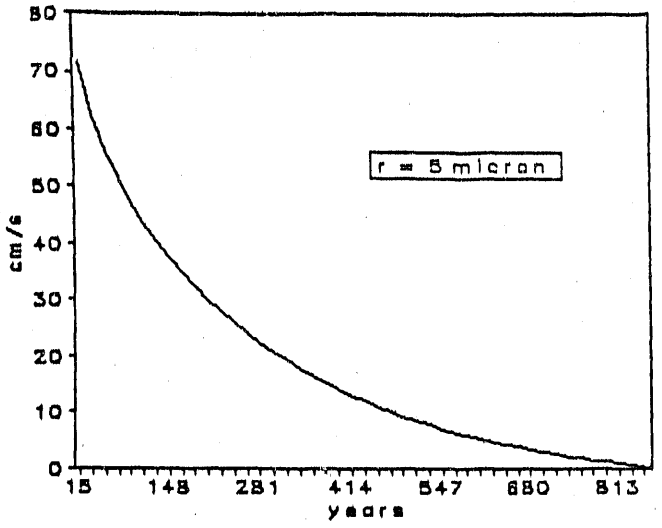
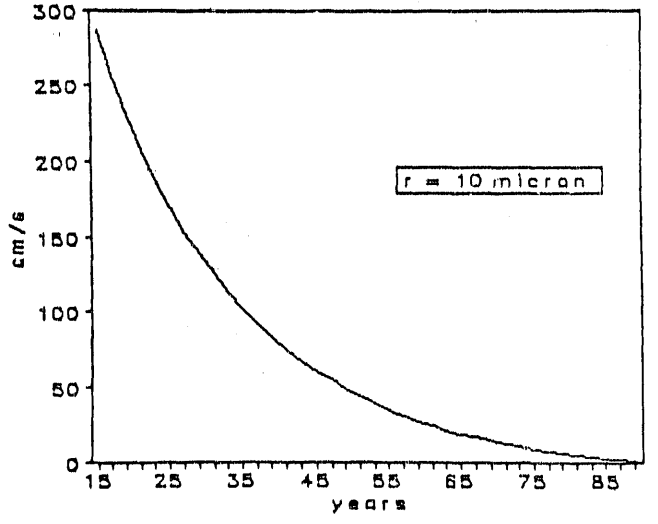


Figure 3. Fill gas fractional release rates until equilibration from 5, 10, and 30 μm radius perforations with breach occurring at t = 15 years (see also footnote 3b).





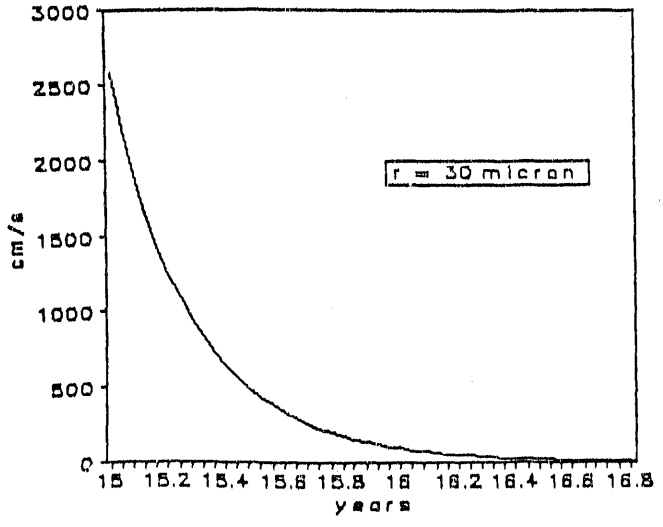


Figure 4. Flow velocity until equilibration within 5, 10, and 30 μm radius perforations with breach occurring at t = 15 years.

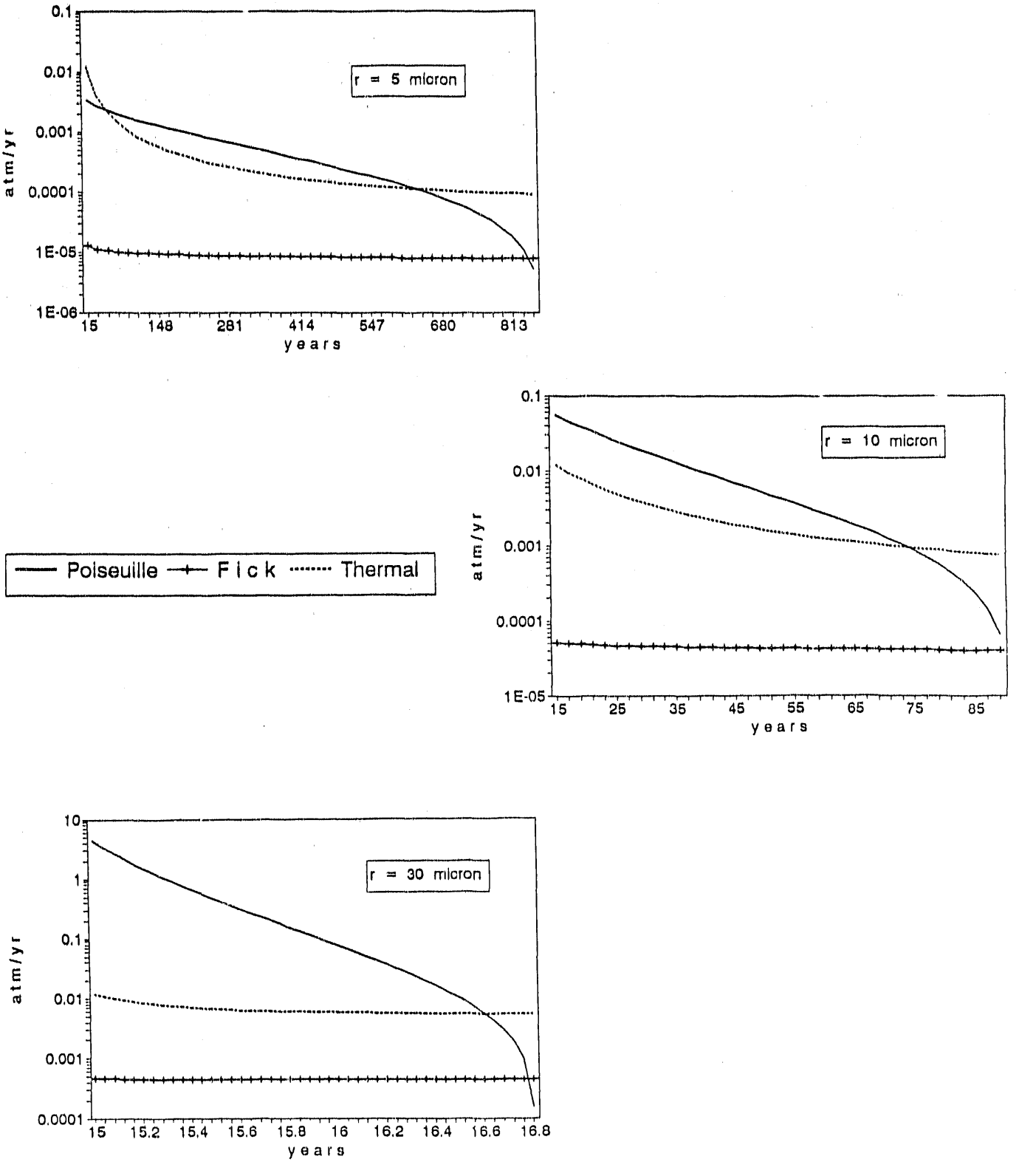


Figure 5. Contributions from Poiseuille flow, fickian diffusion, and temperature decay to the rate of decrease of the internal pressure in the container for 5, 10, and 30 μm radius perforations with breach occurring at t = 15 years.

Poiseuille, fickian (diffusive), and thermal-decay contributions to the internal pressure decrease according to Equation (12).

Under the conditions studied, our results indicate that,

1. the time to equilibration is a strong function of hole radius. Equilibration of inside and outside pressures will be achieved within a year once the radius of the perforation exceeds 35 μm, i.e., ΔP-driven discharges from larger openings (above 35 microns) are characterized by a pulse-type release;

2. for the same ΔP the initial flow velocity increases with the radius. Flow velocities before equilibration are substantial;

3. because flow velocities are substantial, except at the very time of equilibration, the fickian loss term is normally much less than the Poiseuille loss term;

4. the thermal decay pressure term is relatively more important the smaller the hole radius. After equilibration it tends to impose a negative ΔP which is compensated for by air leaking in, which, in turn, keeps the internal pressure practically constant[4].

As shown in Table II, longer times may be required for equilibration if breaches occur later in time. In fact, even if the initial ΔP is smaller, the thermal decay contribution is also smaller (Fig. 6) as the *rate* of change of temperature decreases significantly with time (Fig. 1). On the other hand, because one starts with a smaller ΔP, fewer moles of gas need to be released in order to achieve equilibrium. In any case, with the assumption that the container is backfilled to 1 atm at 25 ^{o}C, 30% to 50% of the fill gas (and therefore ^{14}C impurities[5a]) will be released in equilibrating the pressure. For holes greater than 35μm this would occur in less than a year.

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[4] Our calculations do not exactly apply when P<1 atm. However, the trend they suggest is physically acceptable and to be expected from the mathematical form of Equation (12).

[5a] In order to correlate this with ^{14}C release, the fractional release of Table II, $\Delta n/n_o$, must be multiplied by the fraction of oxidized ^{14}C.

Table II Time-to-pressure-equilibration and fractional amount of gas released as function of different hole radii and breach times.

R [μm]	t_{start} [yr]	Δt_{eq} [yr]	$\Delta n/n_o$
	15	855	0.317
5	300	900	0.298
	600	900	0.282
	15	76	0.407
10	300	100	0.351
	600	104	0.327
	15	1.8	0.478
30	300	1.8	0.362
	600	1.8	0.334

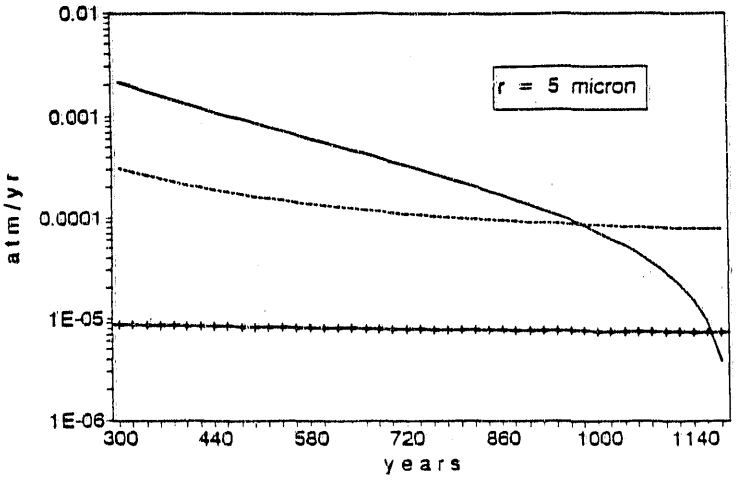
Overall, it can be said that the temperature decrease rate effects on gas release become negligible after approximately 300 hundred years. For such situations, since before equilibration the fickian term in Equation (12) plays also a minor role, an approximate solution to Equation (12) ignoring the fickian and thermal contribution term can be used. Namely:

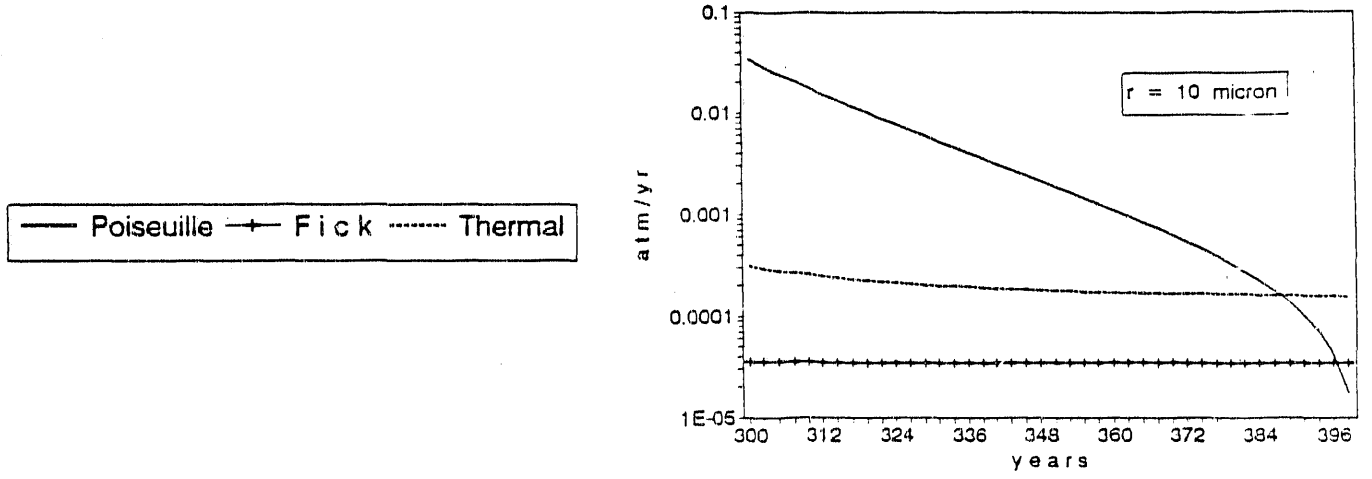
$$P(t) = \frac{P(t_o) + \tanh[I(t)]}{1 + P(t_o) \cdot \tanh[I(t)]} \tag{14a}$$

where:

$$I(t) = \int_{t_o}^{t} \frac{1.1\ \pi r^4}{16\ \mu(t)\ \ell\ V}\, dt \tag{14b}$$

Equations (14a) and (14b) can be further simplified, conservatively (quicker equilibration time), by assuming a constant absolute viscosity of the gas, $\mu(t)$, set equal to the lowest value of the viscosity in the temperature range of interest (Table I).





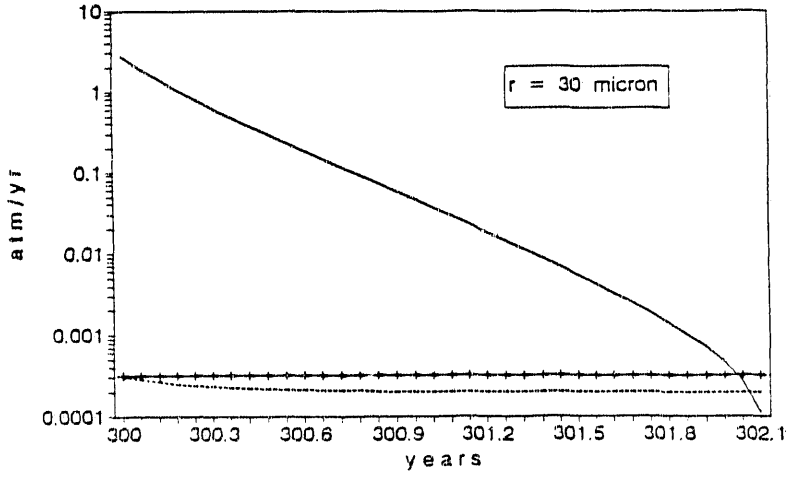


Figure 6. Contributions from Poiseuille flow, fickian diffusion, and temperature decay to the rate of decrease of the internal pressure for containers with 5, 10, and 30 μm radius perforations and breach occurring at t = 300 years.

3.1.2 Partly occluded perforations

Localized corrosion is considered to be the most likely failure mode of spent fuel containers in a wet or humid environment. For iron corrosion products, the molar volume exceeds that of the base metal (Table III). A similar situation would exist with other base metals, e.g., copper. Therefore, the potential exists for the corrosion products to form a well-packed barrier to flow. Small penetrations could also become plugged with particulates deposited by the flowing gas [ANSI, 1987]. To model this, we visualize the perforation as being filled with a porous medium. We treat the porous medium as being comprised of a number of equivalent cylinders of radius, r_i, and length, ℓ_i. Therefore, instead of having a single flow path of length ℓ and radius r, we have a number of paths.

Table III Molar volume of iron and its common corrosion products (Adapted from CRC Handbook of Chemistry, 1981)

Compound	Specific Volume (cm^3) per mole of Fe
Fe	7.11
Fe_3O_4	14.9
$Fe(OH)_2$	26.4
FeO(OH)	20.8
Fe_2O_3	15.25

For a single cylinder, pressure-driven flow is given by the Poiseuille law with a correction for slip (Equations 6 and 7). To obtain the total flow we must sum over all of the different flow paths.

$$Q_p = \sum_{i=1}^{N} \frac{\pi\ (r_i)^4\ \Delta^2 P}{16\ \mu(T)\ \ell_i\ R\ T} \cdot \left(1 + \frac{32\ mfp}{9\ r_i}\right) , \qquad (15)$$

where the subscript p refers to partially occluded perforations.

Recalling Equation (6) and the slip correction Equation (7), the ratio of flow between partially occluded and open perforations is obtained as follows:

$$\frac{Q_p}{Q_o} = \sum_{i=1}^{N} \frac{(r_i/r)^4 \cdot (1 + 32\ mfp/9r_i)}{(\ell_i/\ell) \cdot (1 + 32\ mfp/9r)} \tag{16}$$

In Equation (16), the ratio ℓ_i/ℓ represents the flow reduction due to an increase in the equivalent length. The reduction in flow due to changes in the equivalent length of the channel has been measured for flow through cylinders filled with a variety of porous media with porosities ranging from 0.1 - 0.9 [Carman, 1956; p. 48]. Values for the flow reduction range from 1.1 at the higher porosities to 2 at the lower porosities. Further, it has been noted that the flow reduction "... *undergoes a decided increase, and that, even in unconsolidated beds, the rate of increase probably accelerates rapidly when the porosity < 0.1* ..." [Carman, 1956; p. 49].

From Equation (16) it is obvious that reducing the radius, r_i, leads to a sharp reduction in the flow rate of the partially occluded cylinder as compared to the open one. Furthermore, if there is a distribution of radii, flow will occur primarily in the largest channels because of the proportionality to r^4.

Obtaining the distribution of radii would be an extremely difficult task. Alternatively, to quantify the amount of area that is occluded in terms of a variable which is easier to obtain, we introduce the open porosity of the perforation, ϵ, as the ratio of the empty volume in the partly occluded perforation to that of the open perforation. We also assume, as is normally done, that the flow area varies directly with porosity. In this case,

$$\epsilon = \sum_{i=1}^{N} (r_i/r)^2 \tag{17}$$

If we assume that there are N channels of equal length ℓ_i and equal radius, r_i, the ratio of flow in the occluded channel to that in the open channel becomes:

$$\frac{Q_p}{Q_o} = \frac{\epsilon^2 \ (1 + 32 \ mfp/9r_i)}{N \ (\ell_i/\ell) \cdot (1 + 32 \ mfp/9r)} \tag{18}$$

In Equation (18) the flow ratio is proportional to 1/N, and, thus, the greater the number of channels, the lower the flow for a fixed porosity and uniform distribution of radii. For conservatism, we must choose a single channel, N = 1, with the radius equal to the original radius multiplied by $\epsilon^{1/2}$. This allows the highest flow rate and therefore fastest time to equilibration. With one channel, the equivalent radius is large enough to insure that the slip correction terms become negligible. If we *conservatively* assume that the equivalent length equals the geometric length, the flow rate, Q_p, is upperbounded as follows:

$$Q_p = \epsilon^2 \cdot Q_o \tag{19}$$

where Q_o is now the expression for Poiseuille flow given in Equation (6).

3.2 Post-equilibration releases

3.2.1 Fully open perforations

As indicated earlier, after equilibration of the internal and external pressures is achieved, we conservatively assume that air is the new fill gas and that it is instantly available for oxidation of the ^{14}C. The internal pressure is kept roughly constant by the inflow of air leaking in to compensate for the natural decrease in pressure associated with the decay of the temperature field with time. Upon utilizing a mass balance equation equivalent to Equation (12) implementing both Poiseuille flow and temperature decay rate effects and setting $dP/dt \approx 0$, the following expression for the flow velocity of air leaking in is obtained:

$$u = \frac{V}{\pi r^2} \cdot \frac{1}{T} \cdot \frac{\partial T}{\partial t}, \tag{20}$$

where the temperature profile to be used is that given by Equation (3) expressed in degrees Kelvin. According to Equation (20), the larger

the radius of the opening the smaller is the air inflow velocity. Also, because $\partial T/\partial t$ decreases with time, the inflow velocity is largest at early times.

Having obtained an expression for the air inflow velocity, u, the steady-state outflux of $^{14}CO_2$, $J(x=\ell)$, from a perforated container is derived by solving the one-dimensional diffusion-advection equation:

$$\partial J/\partial x = 0 \tag{21a}$$

with:

$$J(x) = - D\ \partial C/\partial x + uC \tag{21b}$$

and boundary conditions:

$$C(\ell) = 0 \tag{21c}$$

$$C(0) = C_o \tag{21d}$$

The rate of loss of $^{14}CO_2$ per unit area is then:

$$J(x=\ell) = - uC_o \cdot \frac{e^{\alpha}}{1 - e^{\alpha}} \tag{22a}$$

where:

$$\alpha = \frac{u\ell}{D} \tag{22b}$$

Equations (22a) and (22b) have been derived before by Zwahlen [Zwahlen, 1990]. Although the advection velocity, u, is prominent in Equation (22a), it can be easily verified that the flux does become diffusion dominated when $u \to 0$.

Equation (22a) represents the mass loss of $^{14}CO_2$ species from a hole in the container under steady-state release conditions, i.e., in the absence of significant depletion of the $^{14}CO_2$ inventory. Since steady-state conditions are developed on a much faster scale than temperature changes on a repository scale, we utilize Equation (22a) in writing a time-dependent mass balance equation of $^{14}CO_2$ species in a

perforated container. If n(t) is the number of moles of $^{14}CO_2$ in a container at any time t after breach, it is then:

$$\frac{dn}{dt} = - J(x=\ell)\cdot A = \frac{\pi r^2}{V}\cdot u(t)\cdot n(t)\cdot\frac{e^{\alpha(t)}}{1 - e^{\alpha(t)}}, \tag{23a}$$

with:

$$n(t_o) = n_o, \tag{23b}$$

and:

$$\alpha(t) = \frac{u(t)\ \ell}{D(t)}. \tag{23c}$$

Equation (23a) can be solved analytically. In particular, the fractional release rate, Φ, normalized to the initial number of moles, n_o, of $^{14}CO_2$ is expressed as follows:

$$\Phi(t) = \frac{\pi r^2}{V}\cdot u(t)\cdot\frac{e^{\alpha(t)}}{1 - e^{\alpha(t)}}\cdot\exp[\frac{\pi r^2}{V}\ I(t;t_o)] \tag{24a}$$

with:

$$I(t;t_o) = \int_{t_o}^{t} u(\tau)\cdot\frac{e^{\alpha(\tau)}}{1 - e^{\alpha(\tau)}}\ d\tau\ . \tag{24b}$$

The exponential term in Equation (24a) takes into account the effect on release due to the depletion of the $^{14}CO_2$ inventory with time.

In order to obtain the fractional release rate of ^{14}C normalized to the *total* ^{14}C inventory (cladding+structural materials+UO_2 within the spent fuel), it is sufficient to multiply the function $\Phi(t)$ by the oxidized carbon fraction initially present in the container. According to the Yucca Mountain Site Characterization Plan the oxidized ^{14}C fraction, f_{SCP}, available for release at time of breach is:

$$f_{SCP} = \begin{cases} 1\% & \text{for } T > 215\ ^{o}C \\ 0.2\% & \text{for } 170 < T < 215\ ^{o}C \\ 0.1\% & \text{for } T < 170\ ^{o}C \end{cases}$$

In order to account for the extra oxidation of ^{14}C associated with oxygen impurities in the argon gas [Smith, 1989] we shall use instead the following oxidized fraction, f:

$$f = \begin{cases} 2\% & \text{for } T > 215\ ^{o}C \\ 1.2\% & \text{for } T < 215\ ^{o}C \end{cases} \qquad (25)$$

In this equation, T represents the average gas temperature within the container. The results of our calculations for release from fully open perforations are shown in the next section as a special case of release from partly occluded perforations (Figures 7 and 8).

3.2.2 Partly occluded perforations

Post equilibration releases from partially occluded perforations must account for porosity and tortuosity effects. From the expression for post equilibration velocity, Equation (20), it is seen that the velocity is inversely proportional to the area available for flow. This implies that for a fixed area, the velocity is independent of the number of channels. For this reason, we again model the partially occluded perforation in terms of a single, equivalent channel with a radius equal to the original radius multiplied by the square root of the porosity.

With this approach, Equation (20) becomes modified to

$$u_p = \frac{V}{\pi \epsilon r^2} \cdot \frac{1}{T} \cdot \frac{\partial T}{\partial t} = u_o/\epsilon \qquad (26)$$

where r is the radius of the open channel, and u_o is the open channel velocity given in Equation (20). The porosity term causes the area available for flow to decrease. To maintain a constant pressure, the mass flow must be high enough to offset the decrease in pressure caused by the decreasing temperature. Therefore, for a smaller flow area, i.e., smaller porosity, the velocity must increase to maintain the equilibrium pressure.

In a partially occluded perforation, the diffusion path will be longer than in an open hole due to tortuosity. Because viscous flow and diffusion are different processes, the effective increase in path length for diffusion is not necessarily equal to the increase in path length for convection [Carman, 1956; p. 47]. Typical values for the migration length increase, ℓ_{eff}/ℓ, during gaseous diffusion through a porous medium have been found to be in the range of 2 - 8. For one material, this factor was found to have a value of 79 [Youngquist, 1970]. Under diffusion conditions, tortuosity effects are commonly modeled by decreasing the diffusion coefficient, D_o (Equation (2)) by a factor $1/\tau$, with τ the so-called "tortuosity" parameter. The factor $1/\tau$ is the square of the ratio ℓ/ℓ_{eff}. The tortuosity parameter, τ, varies then between 4 and 64, roughly[5].

A conservative correlation that relates the change in tortuosity to porosity and that has been utilized before [Pescatore, 1989] is as follows:

$$\tau = 1 - 4 \log_{10}(\epsilon) \tag{27}$$

while:

$$D_p = D_o/\tau \tag{28}$$

If the porosity is 1, the tortuosity is also 1 and the diffusion coefficient becomes that of an open channel. For a porosity of 1%, the tortuosity is 9.

Using Equations (26) and (28) for u_p and D_p, Equations (23a) - (23c) become:

$$\frac{dn}{dt} = - J(x=\ell)\cdot A_p = \frac{\epsilon \pi r^2}{V}\cdot u_p(t)\cdot n(t)\cdot \frac{e^{\alpha_p(t)}}{1 - e^{\alpha_p(t)}} \tag{29}$$

$$n(0) = n_o \tag{30}$$

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[5] For diffusion of inert, aqueous solutes in porous media τ varies between 2 and 100 [Freeze, 1979].

$$\alpha_p(t) = \frac{u_o(t)\ \ell\ \tau}{D_o(t)\ \epsilon} \tag{31}$$

The normalized fractional release rate expression, Φ_p, that is obtained can be expressed as follows:

$$\Phi_p(t) = \frac{1}{T}\cdot\frac{\partial T}{\partial t}\cdot\frac{e^{\alpha_p(t)}}{1 - e^{\alpha_p(t)}}\cdot\exp\left[\int_{t_o}^{t}\frac{1}{T}\cdot\frac{\partial T}{\partial t}\cdot\frac{e^{\alpha_p(t)}}{1 - e^{\alpha_p(t)}}\cdot dt\right] \tag{32}$$

From these equations it is clear that the porosity and tortuosity only influence the term defined as α_p. However, since α_p appears in the exponentials, it has a significant influence on release. Another way of viewing the influence of tortuosity and porosity is to consider them as making the effective length of the channel longer. In this case,

$$\ell_{eff} = \ell\cdot(\tau/\epsilon) \tag{33}$$

Using ℓ_{eff} along with the flow velocity and diffusion coefficient for open channels gives an equivalent result to modifying the two latter parameters. In fact, the new fractional release rate, Equation (32), is identical to the previous expression for open channels, Equations (24a) and (24b), with the exception that α is now redefined in terms of ℓ_{eff}.

The role of temperature and of its rate of change is explicitly demonstrated in both Equations (26) and (32). Since they also appear in an exponential, releases are sensitive to small changes in these quantities.

Figures 7 to 10 present the results of calculations predicting the fractional release rate of ^{14}C after pressure equilibration from various size perforations as a function of porosity and time of first breach. The calculations are based on Equation (32) multiplied by the oxidized ^{14}C fraction defined in Equation (25). For the temperature profile used, if the initial breach occurs at a time earlier than 120 years, the oxidized fraction is 2%; 1.2% otherwise. Figure 7 shows the results for open perforations (porosity = 1) with radii of 50 and 80 μm with the time of first breach at 15, 100, 250, or 400 years. Figure 8 presents similar results for 100 and 500 μm radius perforations. Figure 9 presents the results for holes with 10% porosity and radii of 100, 500, and 1000 μm and time of first breach at 100, 250, or 400 years. Figure

10 presents analagous results for holes with 1% porosity and a radius of either 500 or 1000 μm.

For the open porosity case, $\epsilon=1$ (Figures 7 and 8), fractional release rates are around 1 part in 10^5 for a 50 μm radius perforation and remain relatively constant for 300 years. As the radius increases, the initial release rate increases. For example, the initial fractional release rate for 100 μm radius holes ranges from 3 to $7 \cdot 10^{-5}$ depending on the failure time. For a 500 μm radius, initially the fractional release rate is around 10^{-3}, and it decreases to less than 10^{-5} after approximately 60 years, due to depletion.

For the 10% porosity case, Figure 9, we simulate breach to occur at 100, 250, and 400 years. For 100 μm radius holes, the fractional release rates are well below 10^{-5} at all times; for the 500 μm radius hole the fractional release rates decrease from 3 to $1 \cdot 10^{-5}$; for the 1000 μm (1 mm) radius holes the fractional release rates decrease from 14 to $2 \cdot 10^{-5}$. *In all cases, releases are approximately two orders of magnitude smaller than for the open porosity case.* Figure 9 also shows that the fractional release rate from 100 μm radius holes with an initial breach at 100 years is substantially *less* than if the initial breach is at 250 or 400 years even though the fraction oxidized is greater. The cause of this effect is found in the expression for the velocity, Equation (26). At early times, the rate of temperature decrease is largest and therefore, the flow velocity (which provides resistance to diffusion) is highest. As the radius increases, the velocity decreases (Equation (26)), therefore, this effect is not observed for the 500 or 1000 μm radius perforations.

For the 1% porosity case, Figure 10, fractional release rates do not exceed $0.5 \cdot 10^{-5}$ for the 1000 μm radius and $0.06 \cdot 10^{-5}$ for the 500 μm radius holes. The fractional releases are accordingly smaller for smaller radii.

The results of this study demonstrate that diffusion against an advective flow can greatly reduce the release rate. This is most evident for small holes because after equilibration, the advective velocity is higher than in large holes, Equation (26). As the hole radius becomes larger, advection becomes less effective in reducing the diffusion rate out of the container. In the limit as advection becomes unimportant, the results previously obtained by Pescatore [Pescatore, 1989, 1990] can be used to determine the maximum hole radius which will still permit controlled release rate limits to be met. In particular,

advection will cease to be important when the magnitude of α_p, Equation (31), is less than 0.1, say. For the diffusion coefficient used, Equation (9), and an initial breach at 15 years, this occurs with a radius of a) 400 μm with a porosity of 1, b) 3,000 μm and a porosity of 0.1, and c) 11,000 μm and a porosity of 0.01.

Under the conditions studied, our findings indicate that, after pressure equilibration,

1. release is a strong function of porosity. Release rates decrease with decreasing porosity as roughly ϵ^2. Fractional release rates are less than $3 \cdot 10^{-5}$ for 50 μm radius holes and 100% porosity, for 500 μm radius holes and 10% porosity, and for 1,000 μm radius holes and 1% porosity;

2. at early times and for holes 100 μm and smaller the inflow of air into the container greatly reduces the release rates of ^{14}C due to diffusion.

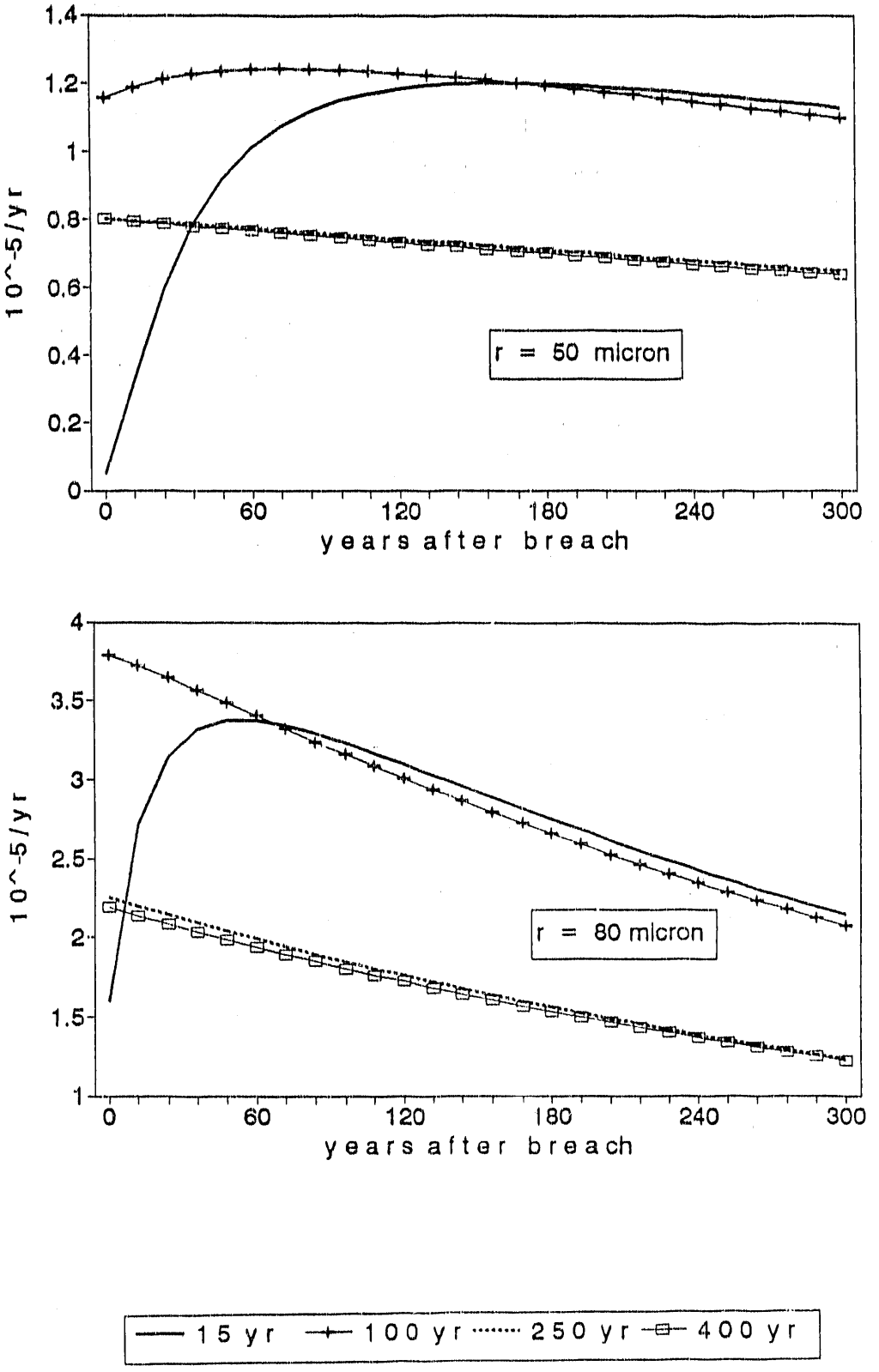

Figure 7. Post-equilibration, fractional release rates of ^{14}C from fully open perforations of 50 and 80 μm radius with breach occurring at 15, 100, 250, and 400 years. Counterflow effectively reduces the release rates for the early failures.

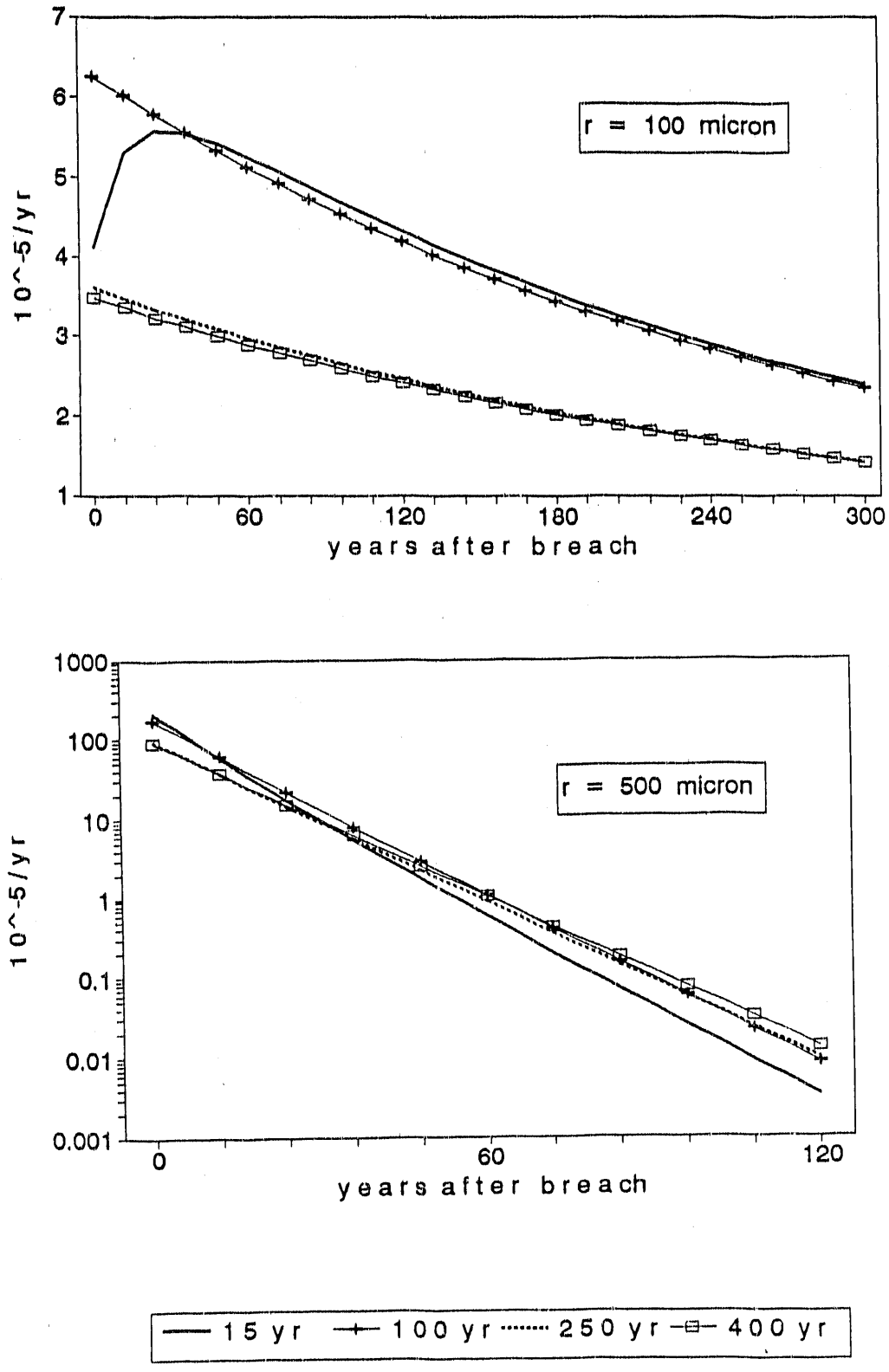

Figure 8. Post-equilibration, fractional release rates of ^{14}C from fully open perforations of 100 and 500 μm radius with breach occurring at 15, 100, 250, and 400 years. Counterflow is not effective in reducing the release rates for 500-μm-radius perforations.

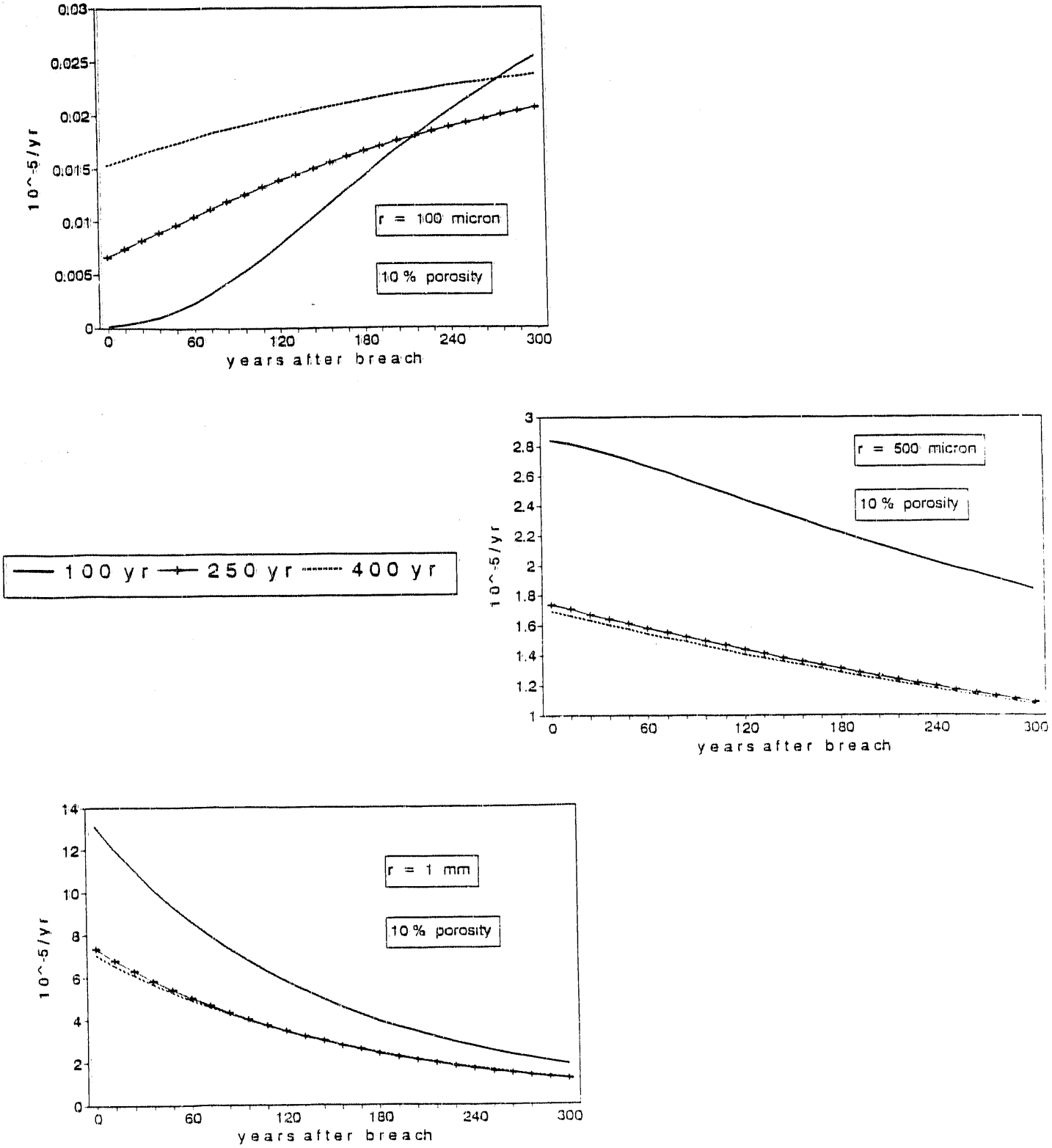

Figure 9. Post-equilibration, fractional release rates of ^{14}C from partly occluded perforation of 100, 500, and 1,000 μm radius with open porosity of 10% and breach occurring at 100, 250, and 400 years. Counterflow effectively reduces the release rates for the early failures only for 100-μm-radius perforations.

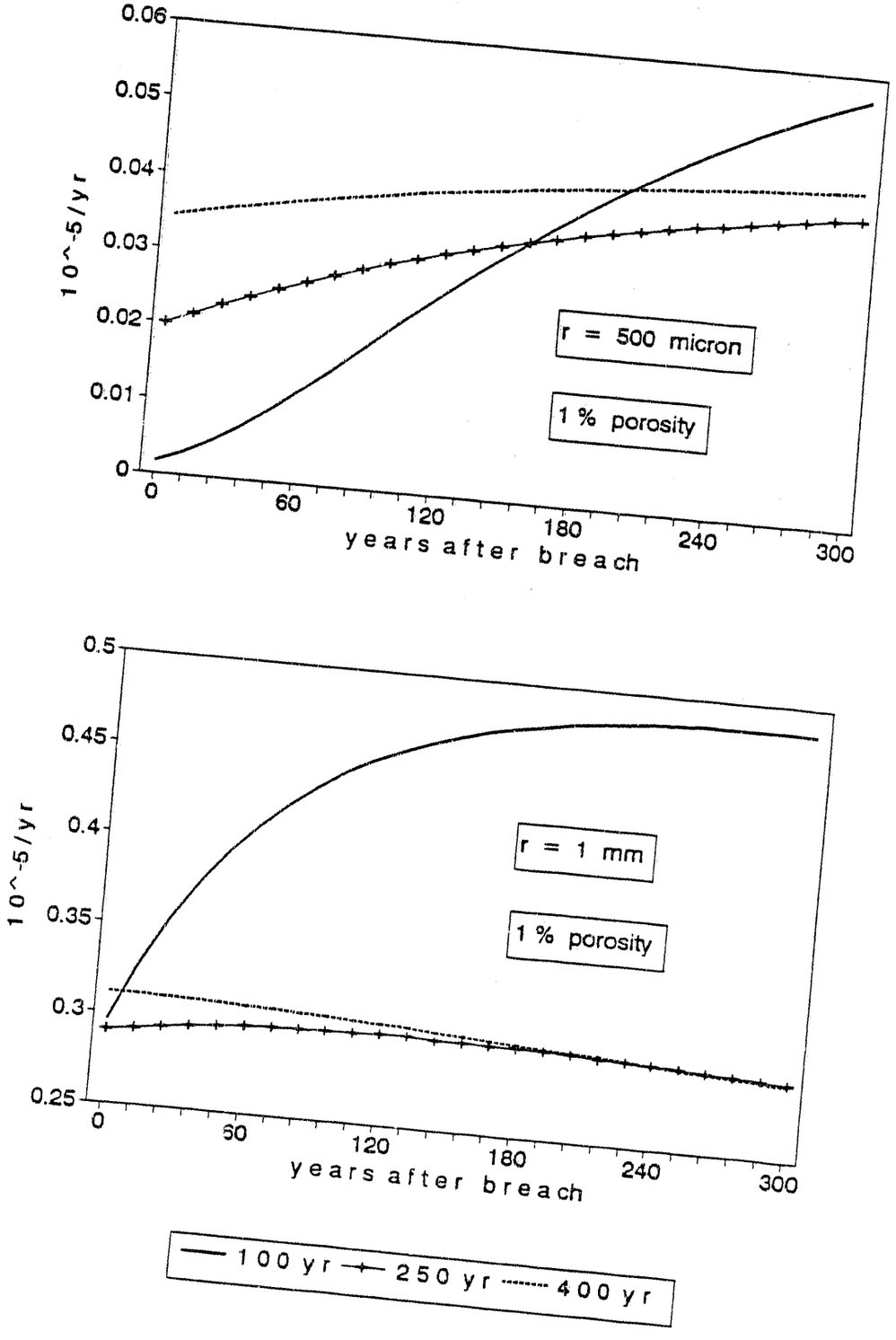

Figure 10. Post-equilibration, fractional release rates of ^{14}C from partly occluded perforations of 500 and 1,000 μm radius with open porosity of 1% and breach occurring at 100, 250, and 400 years. Counterflow effectively reduces the release rates for the early failures only for 500-μm-radius perforations.

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4. DISCUSSION

Underpressurization

An important finding of the previous section is that releases through 50 μm radius holes can be controlled to less than the NRC controlled release rate limit of 1 part in 10^8 of the total inventory[6] provided that the internal gas pressure never exceeds atmospheric. This contrasts with previous studies which did not consider underpressurization [Zwahlen, 1990]. Indeed, if overpressurization is allowed to take place, 5 μm radius holes would cause release rate limits to be violated. This is substantiated in Figures 11 and 12.

Figure 11 presents the fractional release rates from a 50 μm radius open hole in which diffusive release occurs against an advective flow. For this size perforation, equilibration of the inside and outside pressures is practically instantaneous, but an advective flow still exists in order to offset the pressure loss due to the decrease in temperature within the container. In this figure, the fraction of oxidized ^{14}C is 2% for 15 and 100 year initial breach times and 1.2% otherwise. In all cases, the fractional release rate is less than $1.2 \cdot 10^{-5}$ which is lower than the NRC release rate limit[6] of $1.8 \cdot 10^{-5}$.

Figure 12 presents the fractional release rate from a 5 μm radius hole in which release is controlled by advection out of the container. In this example, the pressure inside the container exceeds the outside pressure and argon flows out to equilibrate the pressures. In this case, the fraction of oxidized ^{14}C is 1%, which is lower than in the counterdiffusion example (Fig. 11). In Figure 12, the peak fractional release rate is $1.8 \cdot 10^{-5}$ which is the release rate limit. These results indicate that ΔP-driven discharges are likely to be problematic in terms of licensing because relatively small openings, radius of 5 μm or greater, may have fractional releases of ^{14}C that exceed NRC release rate limits (see also Fig. 3).

In terms of release rates, if indeed significant oxidation of ^{14}C does occur during the inert gas phase, our results demonstrate that it

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[6] Assuming a total 1,000 year inventory of $1.74 \cdot 10^3$ Ci/MTHM [Roddy, 1986] and the most recent estimate for the 1,000 year ^{14}C inventory of 0.97 Ci/MTHM [Van Konynenburg, 1990], it is seen that the ^{14}C fractional release could be approximately $1.8 \cdot 10^{-5}$ and meet the 1 part in 10^8 of the total inventory release rate limit.

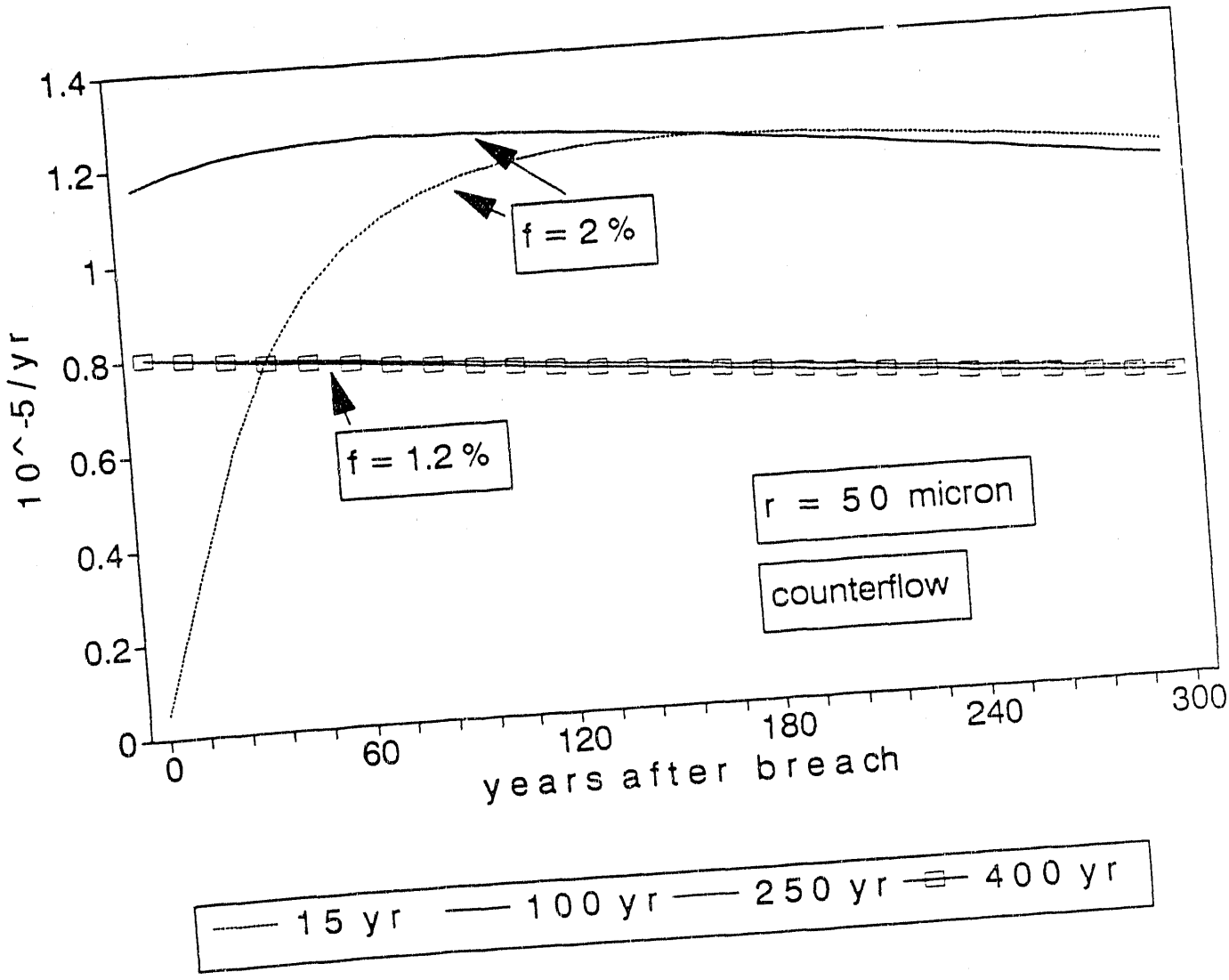


Figure 11. Fractional release rates of ^{14}C from a fully open perforation of 50 μm radius with breach occurring at 15, 100, 250, and 400 years.

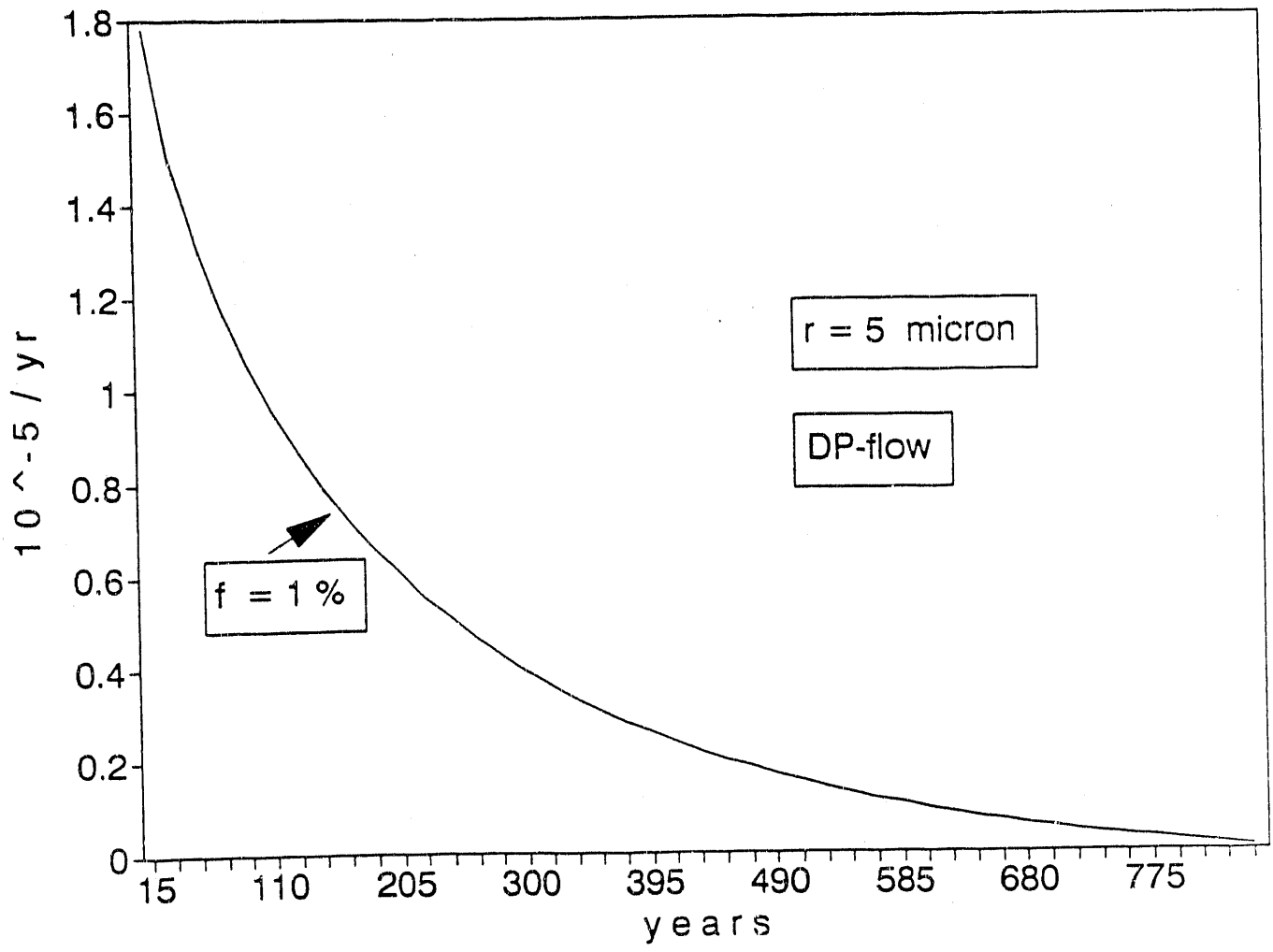


Figure 12. Fractional release rates of ^{14}C from a fully open perforation of 5 μm radius with breach occurring at 15 years.

is worthwhile to cause releases to be controlled by diffusion against a counterflow of air at all times. This could be accomplished by filling the container to a pressure such that, at the peak average fill gas temperature, it would be less than the outside pressure. As the system cools, the internal pressure would decrease further, ensuring that upon breach, flow would be into the container to equilibrate the pressures.

Although it may seem counterintuitive to permit oxygen to flow into the container initially, it will not have a detrimental effect on release for the following reasons. First, for a perforation with a radius of 35 μm or larger, pressure equilibration occurs in 1 year or less. Thus, even if the container is at a higher pressure than the surrounding environment, delay of oxygen entering the container is at most a year. This depressurization step would be characterized by a spiked release (Section 3.1.1), while underpressurization would promote a slow, uniform release (Section 3.2.2). Second, for a smaller radius perforation, if the container is underpressurized with respect to the outside environment, ^{14}C release will occur against a very significant counterflow of air which will cause the NRC release criteria never to be exceeded.

Filling to a lower pressure may cost less but it may also have detrimental effects on other parameters relevant to waste package performance, e.g., heat transfer, leak detection, and ease of fabrication. Decreasing the amount of fill gas in the container will certainly alter convective heat transfer; however, to date, none of the thermal analyses of spent fuel waste packages have considered convection [Sullivan, 1989]. Filling to a lower pressure will not allow sniffing for a gas leak; however, it should not influence ultrasonic and liquid penetrant tests, which "... *represent the best choices for closure certification* [Day, 1988]. The ease of fabrication for a spent fuel waste container may be adversely affected if underpressurization is used. For example, friction welding may no longer be considered and it may prove difficult to maintain a partial vacuum within the container and in the hot cell. Other possible consequences of having a lower fill gas pressure should be examined before proceeding.

Although we recommend underpressurization as a means of reducing the pulse type of release associated with pressure equilibration, the advantage gained in underpressurizing the container may be significantly reduced if the oxidized fraction of the <u>*total*</u> ^{14}C inventory is significantly less than our assumed value of up to 2%. Release is directly proportional to the oxidized fraction.

Meeting Regulatory Release Limits

Limiting gaseous releases by diffusion against air flowing into the container also offers some hope in demonstrating that substantially complete containment can be met. DOE has proposed to reduce release rate limits by a factor of 10 during the substantially complete containment period. This allows two possible release rate limits: a) 10^{-6} of the ^{14}C 1,000 year inventory, and b) 10^{-9} of the total 1,000 year inventory which is $1.8 \cdot 10^{-6}$ of the ^{14}C 1,000 year inventory. Our previous results, Figures 7 - 10, can be used to estimate the *cumulative* fraction of failed containers that could be tolerated while meeting the release limit. The results are presented in Table IV which provides the cumulative percentage of failed containers as a function of release rate limit, hole size and porosity.

Design goals have been set for the number of container failures per year [DOE, 1988] in order to meet the substantially complete containment and controlled release criteria. These are reproduced in Figures 13 and 14. During the substantially complete containment period, the maximum fractional container failure rate, f_c, is

for: $t < 100$ yr; $f_c < 0.0001$/yr
for: $100 < t < 300$ yr; $f_c < 0.0005$/yr
for: $300 < t < 1000$ yr; $f_c < 0.001$/yr

If the maximum failure rate was obtained every year, 1% of the containers would fail in 100 years, 11% in 300 years, and 81% in 1000 years. For a substantially complete containment period of 300 years, this would require open perforations with a radius of 50 μm or 500 μm radius holes filled to 10% porosity.

It is not likely that the Yucca Mountain Project would plan for the container design to hit the maximum failure rate every year. In Figure 13, it is stated that "*...the potential fraction of total failures will be determined as part of the container material studies and will be consistent with regulatory intent.*" If the cumulative fraction of container failures were less than reported above, larger radius holes could be tolerated while still meeting controlled release limits. For example, if only roughly 1% to 2% of the containers were to

TABLE IV Maximum, allowable cumulative fraction of failed containers as a function of hole size, porosity (ϵ), and release rate limit.

Radius [μm]	Diameter [mm]	Max % Failed FRR[1] = 10^{-6}	Max % Failed FRR = $1.8 \cdot 10^{-6}$
		ϵ = 1	
50	0.1	8 - 13†	14 - 23
80	0.16	3 - 5	5.4 - 9
100	0.2	1.5 - 3	2.7 - 5.4
		ϵ = 0.1	
100	0.2	50 - 100	100
500	1.0	3.5 - 5.5	6.3 - 10
1000	2.0	0.8 - 1.4	1.4 -2.6
		ϵ = 0.01	
500	1.0	100	100
1000	2.0	33 - 50	60 - 90

[1] FRR = Fractional Release Rate normalized to 1,000 year ^{14}C inventory.

† Range of fraction failed is due to different failure times. For failures at less than 100 years, the fraction of oxidized ^{14}C is assumed to be 2%, after 100 years it is 1.2%. Lower failure rates are required for breach times less than 100 years.

fail during the substantially complete containment period 1000 μm radius (2-mm diameter) holes with 10% porosity could be tolerated.

A further significant advantage of controlling release by advection against a counterflow of air is that for open perforations with a radius of less than 500 μm, the pulsed release associated with advective flow out of the container is removed. Initial releases are much lower and tend to remain relatively constant with time, Figures 7 - 10. This may be used to remove limitations on fractional container failure rates. For a constant release rate, only the cumulative number of container failures needs to be known. Defining a maximum cumulative number of failures over time will be easier than defining a maximum rate of failures over the same time.

Release from Multiple Perforations

We recommend that releases be modeled using a single, equivalent perforation as opposed to summing up releases from many smaller perforations. During the pressure equilibration phase this is a conservative assumption (see modeling assumptions section). Also, during the phase when diffusive release occurs against a counter flow of air, release is dependent only upon the available perforated area and not on the number of channels. This can be demonstrated by examining the equation for fractional release from containers with a porous medium in the perforation, Eqn. (32). The only term dependent on the radius of the perforation is α_p which depends on the velocity. However, the velocity is dependent on the total perforated area and not the number or size of the channels.

Modeling Assumptions

The results in this document rest upon a number of assumptions. Every attempt was made to provide conservative (but not not overly conservative) results. This was accomplished through choice of conservative models and parameters.

In model development, several choices were made to ensure conservative predictions would result. For example, during the pressure equilibration phase for perforations filled with corrosion products, a single equivalent channel was modeled. If we had allowed for a number of smaller channels, the mass flow, which is proportional to r^4, would have been lower. Therefore, release rates would be lower and time to equilibration would be longer. Also, fickian

Figure 13 Reference approach for Issue 1.4 (containment by waste package) [DOE, 1988].

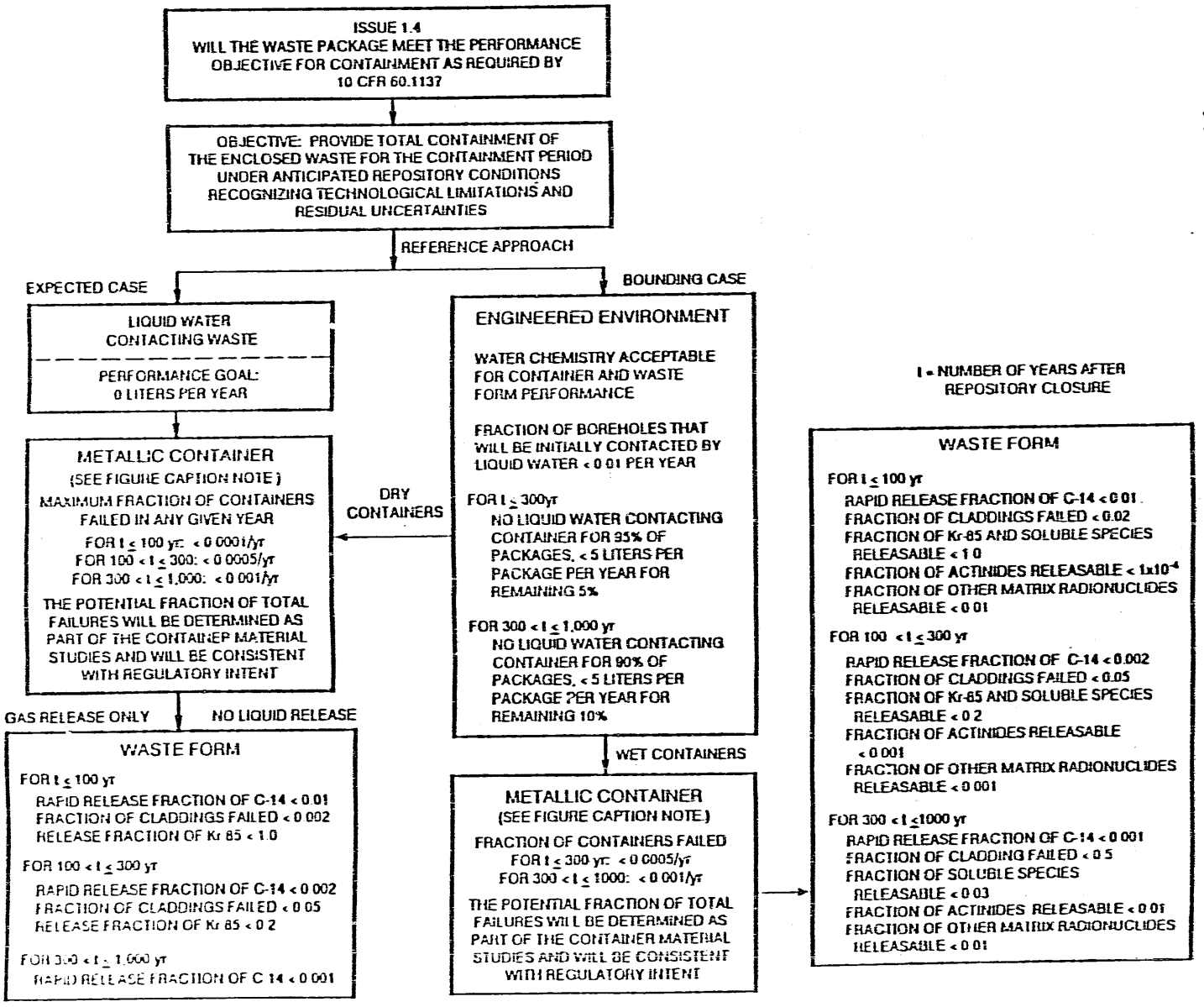
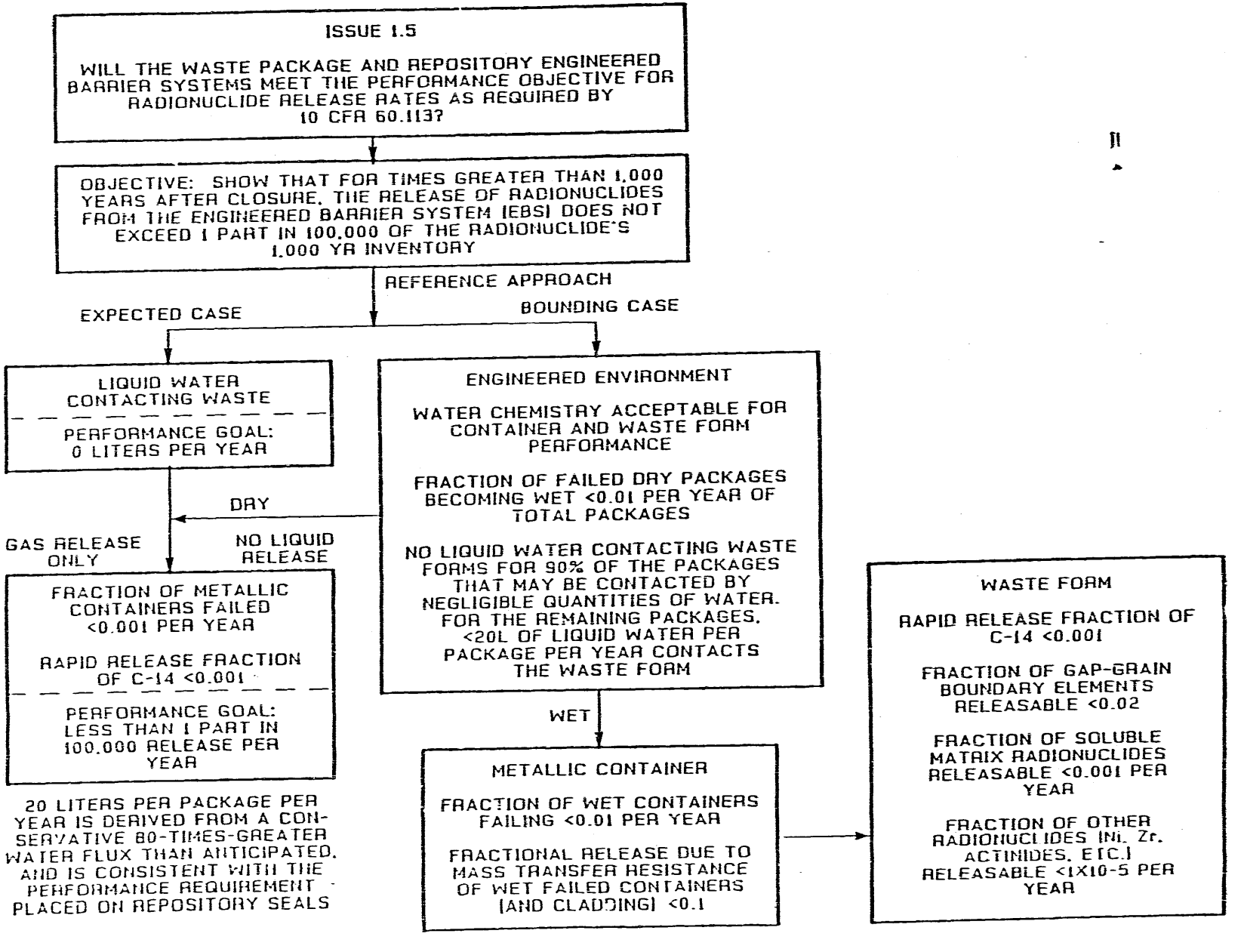


Figure 14 DOE's Reference approach to resolving Issue 1.5 [DOE, 1988].



diffusion was modeled during pressure equilibration. This leads to slightly earlier equilibration times.

The assumptions about two key parameters, temperature and oxidized fraction of ^{14}C, were made to provide conservative upper bounds on release but warrant further investigation. First, in our work, the thermal history for each container is the same and is assumed to be identical with the hottest package in the proposed repository. Containers near the edge of the repository will see a substantially different thermal history [Nelson, 1989]. Releases are sensitive to the temperature at breach and the thermal history of the package, Equation (32). Assuming hotter temperatures leads to higher fractions of oxidized ^{14}C, higher diffusion coefficients, and higher advection velocities. All of these influence release rates. Second, the oxidized fraction of ^{14}C is assumed to be 1% in an argon atmosphere plus another 1% if the average gas temperature is above 215 ^{o}C at time of breach or 0.2% otherwise. Fractional release rates scale directly with the oxidized fraction.

Relaxation of the EPA and NRC ^{14}C Release Limits

Finally, it is recognized that the release rate limits on ^{14}C are extremely stringent [Park, 1990; Van Konynenburg, 1990]. The NRC controlled release limit of 1 part in 10^8 of the total inventory allows only 1.22 Ci/yr to be released. In comparison, typical releases from operating nuclear power plants are approximately 10 Ci/yr per GW(e) [NCRP, 1985]. However, even if releases from the waste package were limited to 1.22 Ci/yr, if all of the ^{14}C ends up in the atmosphere, the EPA limit of a total release of 0.1 Ci/MTHM of ^{14}C over 10,000 years, (7000 Ci for a 70,000 MTHM repository) will be exceeded. Further thought should be given to obtaining a relaxation in the release rate limits of NRC and EPA. If the EPA were to increase its release rate limit by an order of magnitude, approximately 100% of the ^{14}C inventory (based on Van Konynenburg's estimated inventory, see footnote on page 1) could be released over 10,000 years.

5. CONCLUSIONS

The potential release of gaseous $^{14}CO_2$ from small perforations in waste containers has been evaluated as a function of temperature, hole size, open porosity within the hole, and time, based on the waste package design parameters and environmental conditions described in the Yucca Mountain Site Characterization Plan.

The analysis has been performed by breaking the release problem into two time domains. In the first time domain a positive ΔP between the argon fill gas and outside air drives the former out of the spent fuel container (type-1 conditions). The flow regime is essentially of the Poiseuille type for compressible gases. By the time equilibration of the inside and outside pressure is achieved, 30 to 50% of the argon gas and of the $^{14}CO_2$ inventory (modeled as an impurity in the argon gas) are released. Equilibration will take less than a year for 35 μm radius perforations and larger. For these perforations the release of $^{14}CO_2$ can be characterized as a spiked release. Following pressure equilibration, air is assumed to be the new fill gas instantly oxidizing the exposed ^{14}C. In this time domain $^{14}CO_2$ counterdiffuses against the inflow of air leaking into the container in order to offset the natural decrease in pressure due to the decay in the temperature field (type-2 conditions). The inflow of air is significant for perforations of 100 μm radius and smaller, and it is most important at early times. This type of flow regime is characterized by relatively uniform releases over time. In both time domains we have utilized conservative assumptions regarding modeling itself and the environmental parameter values to be used, e.g., we considered a temperature-versus-time profile more typical of the hottest containers, whereas it is known that edge effects at the time of emplacement will cause smaller temperature increases.

The $^{14}CO_2$ release models presented in this report can and should be used for analyzing the potential of present container designs to meet the EPA and NRC regulations. An important conclusion already apparent from the present work is that, if indeed significant oxidation of the ^{14}C takes place during the inert gas phase, an incentive exists to originally underpressurize the containers so that a negative ΔP will always exist at time of breach. This will ensure that type-2 conditions will prevail avoiding spiked releases, removing small-size perforations (35-μm radii and smaller, say) from the list of potential offenders, and resulting in the smallest releases at early times when the release criteria are strictest. In particular, assuming (a) a cumulative fraction of failed containers of roughly 1% to 2% during the

substantially complete containment period, (b) initial underpressurization of the fill gas, and (c) an oxidized fraction of 2% of the total ^{14}C inventory, perforation diameters of the order of 0.2 mm, if totally open holes, or of 2 mm, for holes with a porosity of 10%, will allow meeting a release rate criterion ten times stricter that the NRC controlled release criterion.

Alternatively, our analysis helps provide the basis for requesting changes in the regulations if it is found impossible to demonstrate with reasonable assurance that the perforation area will be limited to such low levels as the present regulations require. This might prove eventually to be the case given the current state-of-the-art in modeling corrosion processes and given the foreseeable uncertainties in establishing the potential environment to which the spent fuel containers will be exposed.

In any event, it is recognized that the release rate limits on ^{14}C from a HLW repository are extremely stringent and not in line with the criteria applicable to other phases of the nuclear fuel cycle. Therefore, it would be advisable to request a relaxation of the EPA release criterion for ^{14}C by one order of magnitude or slightly more. This could allow up to 100% of the ^{14}C inventory to be released to the accessible environment without licensing penalties.

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